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(54) Title: ANTIRELECTIVE COATING COMPOSITIONS

(57) Abstract: Antireflective coatings and related polymers are disclosed.

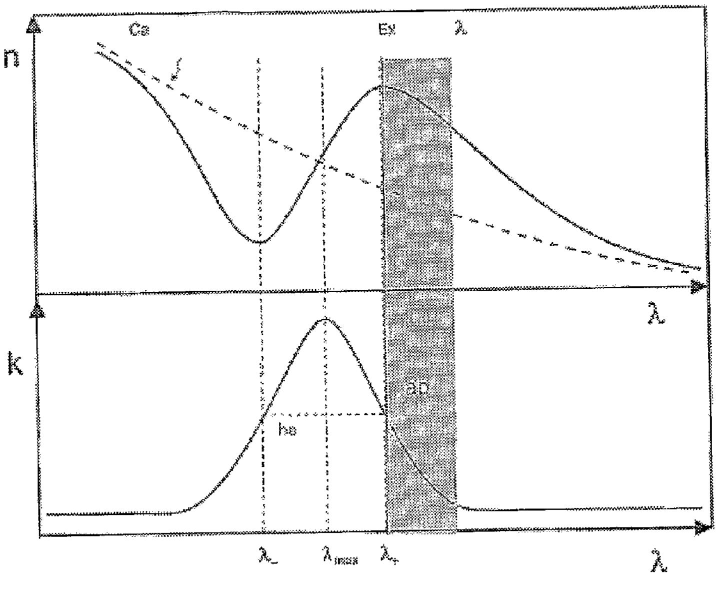

Fig. 1

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Antireflective Coating Compositions

Field of Invention

The present invention relates to a novel antireflective coating composition and its use in image processing by forming a thin layer of the novel antireflective coating composition between a reflective substrate and a photoresist coating. Such compositions are particularly useful in the fabrication of semiconductor devices by photolithographic techniques.

Background

Photoresist compositions are used in microlithography processes for making miniaturized electronic components such as in the fabrication of computer chips and integrated circuits. Generally, in these processes, a thin coating of film of a photoresist composition is first applied to a substrate material, such as silicon wafers used for making integrated circuits. The coated substrate is then baked to evaporate any solvent in the photoresist composition and to fix the coating onto the substrate. The baked coated surface of the substrate is next subjected to an image-wise exposure to radiation.

This radiation exposure causes a chemical transformation in the exposed areas of the coated surface. Visible light, ultraviolet (UV) light, electron beam and X-ray radiant energy are radiation types commonly used today in microlithographic processes. After this image-wise exposure, the coated substrate is treated with a developer solution to dissolve and remove either the radiation-exposed or the unexposed areas of the photoresist.

The trend towards the miniaturization of semiconductor devices has led to the use of new photoresists that are sensitive to lower and lower wavelengths of radiation and has also led to the use of sophisticated multilevel systems to overcome difficulties associated with such miniaturization.

The use of highly absorbing antireflective coatings in photolithography is one approach to diminish the problems that result from back reflection of light from highly reflective substrates. Two major disadvantages of back reflectivity are thin film interference effects and reflective notching. Thin film interference, or standing waves, and changes in critical line width dimensions caused by variations in the total light intensity in the photoresist film as the thickness of the photoresist changes. Reflective notching becomes severe as the photoresist is patterned over substrates containing topographical features, which scatter light through the photoresist film, leading to line width variations, and in the extreme case, forming regions with complete photoresist loss.

In cases where further reduction or elimination of line width variation is required, the use of bottom antireflective coating provides the best solution for the elimination of reflectivity. The bottom antireflective coating is applied to the substrate prior to coating with the photoresist and prior to exposure. The photoresist is exposed imagewise and developed. The antireflective coating in the exposed area is then etched, typically in gaseous plasma, and the photoresist pattern is thus transferred to the substrate. The etch rate of the antireflective film should be relatively high in comparison to the photoresist so that the antireflective film is etched without excessive loss of the photoresist film during the etch process. Antireflective coatings must also possess the correct absorption and refractive indices (known as 'k' and 'n') at the wavelength of exposure to achieve the desired lithographic properties.

It is necessary to have a bottom antireflective coating that functions well at exposures less than 300 nm. Such antireflective coatings need to have high etch rates and be sufficiently absorbing with the correct refractive index to act as antireflective coatings.

SUMMARY OF THE INVENTION

The invention describes an antireflective coating composition which contains a novel polymer without an aromatic chromophore, which finds applications in anti-reflective coating materials in high NA lithography. The materials have ultra high etch rates because of the polymer backbone and the absence of aromatic chromophore attached to the polymer.

The antireflective coating composition of the present invention comprises a polymer which does not contain an aromatic chromophore, an acid generator, and optionally a crosslinking agent, where the polymer comprises a structural unit derived from an aminoplast and a structural unit derived from a diol, triol, dithiol, trithiol, other polyols, diacid, triacid, other polyacids, diimide, diamide, imide-amide, or mixture thereof, where the diol, dithiol, triol, trithiol, diacid, triacid, diimide, diamide, or imide-amide optionally contain one or more nitrogen and/or sulfur atoms or contain one or more alkene groups to improve absorbtivity at a wavelength useful in IC manufacturing and achieve high n value for the antireflective material.

The present invention is also related to a polymer which does not contain an aromatic chromophore comprising a structural unit derived from an aminoplast and a structural unit derived from a diol, triol, dithiol, trithiol, other polyols, diacid, triacid, other polyacids, diimide or mixture thereof, where the diol, dithiol, triol, trithiol, diacid, triacid, diimide, diamide, or imide-amide optionally contain one or more nitrogen and/or sulfur atoms or contain one or more alkene groups.

The present invention also relates to a coated substrate comprising a substrate having thereon an antireflective coating layer formed from the antireflective coating composition disclosed herein, where the antireflective coating layer has an absorption parameter (k) in the range of $0.01 \leq k < 0.35$ when measured at 193 nm. In addition, the present invention also relates to a process for forming an image comprising, a) coating and baking a substrate with the antireflective coating composition disclosed herein; b) coating and baking a photoresist film on top of the antireflective coating; c) imagewise exposing the photoresist; d) developing an image in the photoresist; e) optionally, baking the substrate after the exposing step. In addition, the present invention also relates to a process for forming on a substrate an antireflective film and a photoresist film sensitive to an exposure wavelength, comprising a) forming an antireflective film on a substrate, where the antireflective film is formed from the antireflective coating composition of the present invention where the diol, triol, dithiol, trithiol, diacid, triacid diimide, diamide, or imide-amide in the antireflective coating composition is chosen in such a way that the absorption maximum of the polymer in the antireflective coating composition is less than the exposure wavelength for the photoresist and where the exposure wavelength is between the absorption maximum and the absorption minimum on the long wavelength side of the absorption band of the polymer in the antireflective coating composition, resulting in an anomalous dispersion contribution to the refractive index of the antireflective film that raises the refractive index 'n' of the antireflective film and lowers the absorption parameter 'k' of the antireflective film; and b) forming the photoresist film on top of the antireflective film. In some instances, the diol, triol, dithiol, trithiol, other polyols, diacid, triacid, other polyacids, diimide, diamide, or imide-amide can be chosen such that the absorption maximum of the polymer in the antireflective coating composition is less than the exposure wavelength for the photoresist and where the exposure wavelength is between the half height of the absorption band of the polymer in the antireflective coating composition and the absorption minimum on the long wavelength side.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates the principle of anomalous dispersion with the following meanings:

Ca: Cauchy correlations
Ex λ: Exposure λ (high n low k region)
ab: absorption band
ha: half measure

Fig. 2 shows dispersion curves showing anomalous dispersion effect for coating example 2, measured by spectroscopic ellipsometry. wa denotes wavelength.

DETAILED DESCRIPTION OF THE INVENTION

The invention describes an antireflective coating composition which contains a novel polymer without an aromatic chromophore, which finds applications in anti-reflective coating materials in high NA lithography. The materials have ultra high etch rates because of the polymer backbone and the absence of aromatic chromophore attached to the polymer.

The antireflective coating composition of the present invention comprises a polymer which does not contain an aromatic chromophore, an acid generator, and optionally a crosslinking agent, where the polymer comprises a structural unit derived from an aminoplast and a structural unit derived from a diol, triol, dithiol, trithiol, other polyols, diacid, triacid, other polyacids, diimide, diamide, imide-amide, or mixture thereof, where the diol, dithiol, triol, trithiol, diacid, triacid, diimide, diamide, or imide-amide optionally contain one or more nitrogen and/or sulfur atoms or contain one or more alkene groups.to improve absorbtivity at a wavelength useful in IC manufacturing and achieve high n value for the antireflective material.

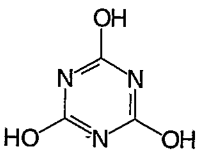
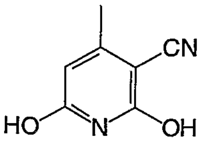
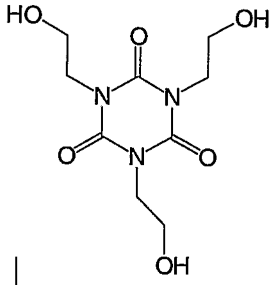
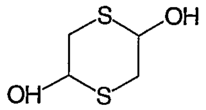
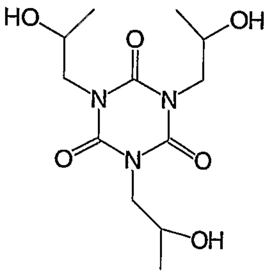
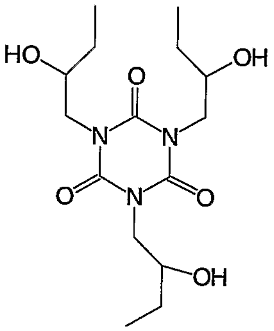
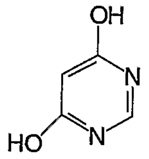
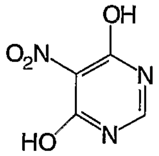
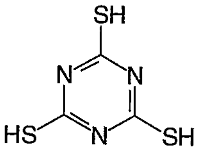
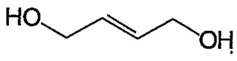
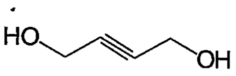
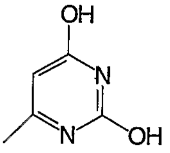
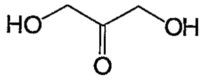
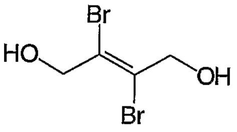
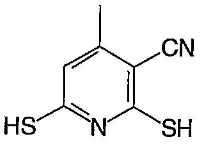
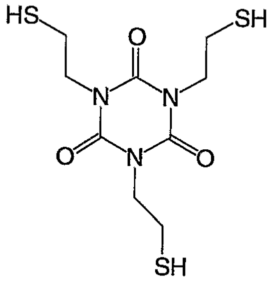
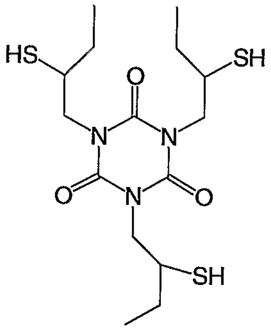
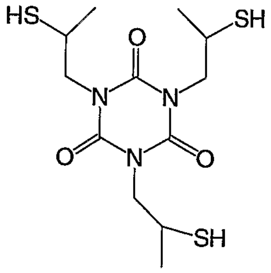
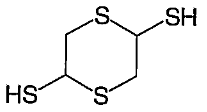
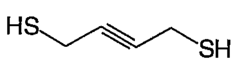
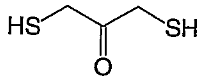
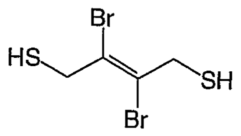
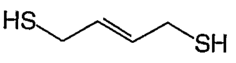
The present invention is also related to a polymer which does not contain an aromatic chromophore comprising a structural unit derived from an aminoplast and a structural unit derived from a diol, triol, dithiol, trithiol, other polyols, diacid, triacid, other polyacids, diimide or mixture thereof, where the diol, dithiol, triol, trithiol, diacid, triacid, diimide, diamide, or imide-amide optionally contain one or more nitrogen and/or sulfur atoms or contain one or more alkene groups.

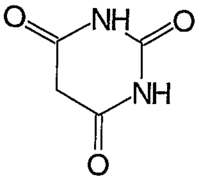
The present invention also relates to a coated substrate comprising a substrate having thereon an antireflective coating layer formed from the antireflective coating composition disclosed herein, where the antireflective coating layer has an absorption parameter (k) in the range of $0.01 \leq k < 0.35$ when measured at 193 nm. In addition, the present invention also relates to a process for forming an image comprising, a) coating and baking a substrate with the antireflective coating composition disclosed herein; b) coating and baking a photoresist film on top of the antireflective coating; c) imagewise exposing the photoresist; d) developing an image in the photoresist; e) optionally, baking the substrate after the exposing step.

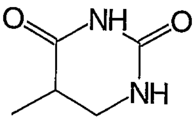
The present invention also relates to a coated substrate comprising a substrate having thereon an antireflective coating layer formed from the antireflective coating composition disclosed herein, where the antireflective coating layer has an absorption parameter (k) in the range of $0.01 \leq k < 0.35$ when measured at 193 nm. In addition, the present invention also relates to a process for forming an image comprising, a) coating and baking a substrate with the antireflective coating composition disclosed herein; b) coating and baking a photoresist film on top of the antireflective coating; c) imagewise exposing the photoresist; d) developing an image in the photoresist; e) optionally, baking the substrate after the exposing step. In addition, the present invention also relates to a process for forming on a substrate an antireflective film and a photoresist film sensitive to an exposure wavelength, comprising a) forming an antireflective film on a substrate, where the antireflective film is formed from the antireflective coating composition of present invention where the diol, triol, dithiol, trithiol, diacid, triacid diimide, diamide, or imide-amide in the antireflective coating composition is chosen in such a way that the absorption maximum of the polymer in the antireflective coating composition is less than the exposure wavelength for the photoresist and where the exposure wavelength is between the absorption maximum and the absorption minimum on the long wavelength side of the absorption band of the polymer in the antireflective coating composition, resulting in an anomalous dispersion contribution to the refractive index of the antireflective film that raises the refractive index 'n' of the antireflective film and lowers the absorption parameter 'k' of the antireflective film; and b) forming the photoresist film on top of the antireflective film. In some instances, the diol, triol, dithiol, trithiol, other polyols, diacid, triacid, other polyacids, diimide, diamide, or imide-amide can be chosen such that the absorption maximum of the polymer in the antireflective coating composition is less than the exposure wavelength for the photoresist and where the exposure wavelength is between the half height of the absorption band of the polymer in the antireflective coating composition and the absorption minimum on the long wavelength side.

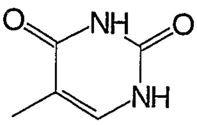
As used herein, aromatic chromophore means an arene containing chromophore that contains only carbon atoms in the ring structures; for example, phenyl, naphthyl, and the like.

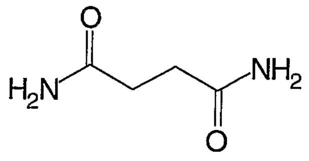
Examples of the diols, triols, dithiols, trithiols, diacids, triacids, and diimide include, for example,

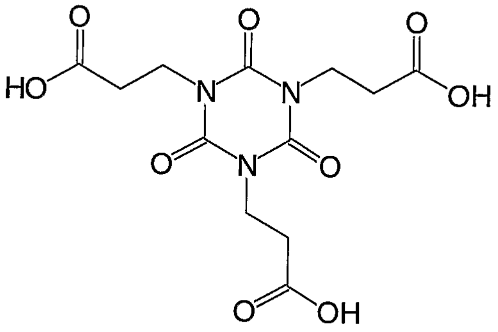
























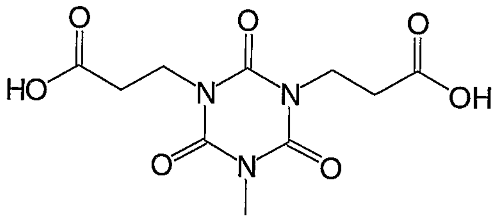


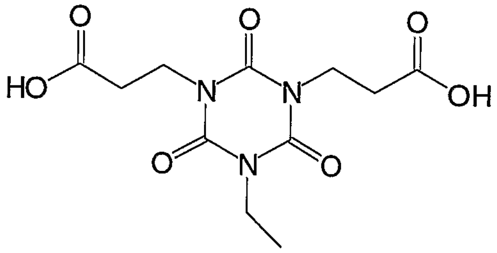


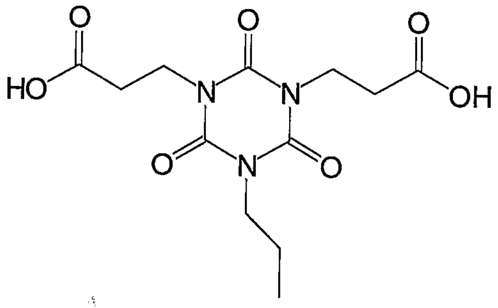


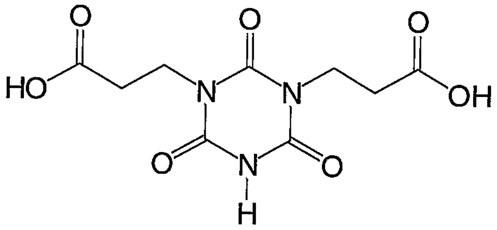


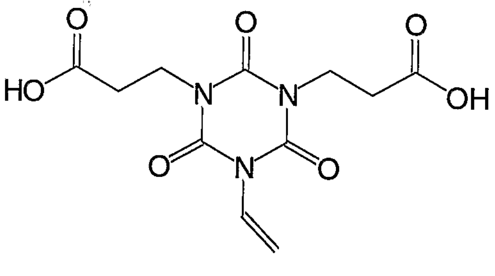








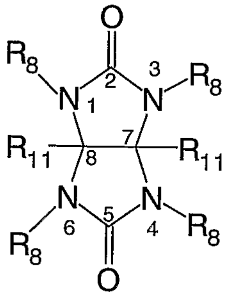




, and the like.

The polymer of the present invention is self-crosslinkable with assistance of an acid generator.

The aminoplast can be substituted by two or more alkoxy groups can be based on aminoplasts such as, for example, glycoluril-aldehyde resins, melamine-aldehyde resins, benzoguanamine-aldehyde resins, and urea-aldehyde resins. Examples of the aldehyde include formaldehyde, acetaldehyde, etc. In some instances, three or four alkoxy groups are useful. Monomeric, alkylated glycoluril-formaldehyde resins are an example. One example is tetra(alkoxyalkyl)glycoluril having the following structure



(A)

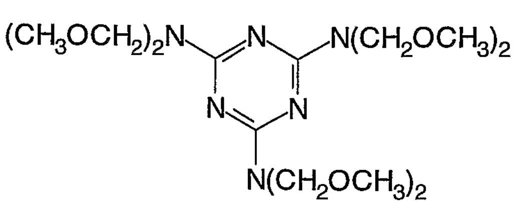
where each R_8 is $(CH_2)_n{-}O{-}(CH_2)_m{-}CH_3$, each R_{11} is hydrogen or C_1-C_6 alkyl, n is 1 to 4, and m is 0 to 3.

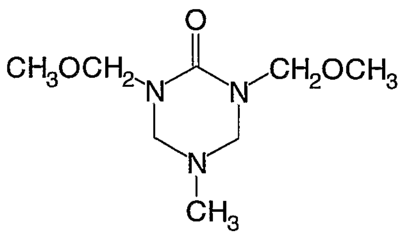
(the numbers in (A) indicating atom number for compound naming)

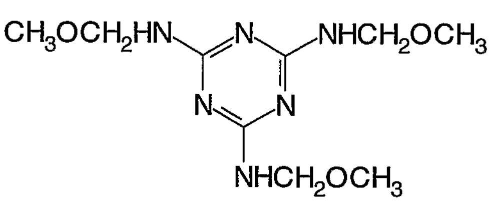
Examples of tetra(alkoxymethyl)glycoluril, may include, e.g., tetra(methoxymethyl)glycoluril, tetra(ethoxymethyl)glycoluril, tetra(n-propoxymethyl)glycoluril, tetra(i-propoxymethyl)glycoluril, tetra(n-butoxymethyl)glycoluril, tetra(t-butoxymethyl)glycoluril, substituted tetra(alkoxymethyl)glycolurils such as 7-methyl tetra(methoxymethyl)glycoluril, 7-ethyl tetra(methoxymethyl)glycoluril, 7-(i- or n-)propyl tetra(methoxymethyl)glycoluril, 7-(i- or sec- or t-)butyl tetra(methoxymethyl)glycoluril, 7,8-dimethyl tetra(methoxymethyl)glycoluril, 7,8-diethyl tetra(methoxymethyl)glycoluril, 7,8-di(i- or n-)propyl tetra(methoxymethyl)glycoluril, 7,8-di(i- or sec- or t-)butyl tetra(methoxymethyl)glycoluril, 7-methyl-8-(i- or n-)propyl tetra(methoxymethyl)glycoluril, and the like. Tetra(methoxymethyl)glycoluril is available under the trademark POWDERLINK from Cytec Industries (e.g., POWDERLINK 1174). Other examples include methylpropyltetramethoxymethyl glycoluril, and methylphenyltetramethoxymethyl glycoluril.

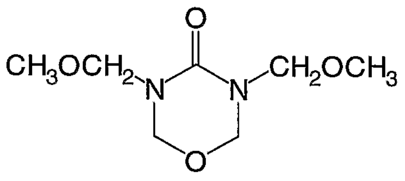
Other aminoplasts are commercially available from Cytec Industries under the trademark CYMEL and from Monsanto Chemical Co. under the trademark RESIMENE. Condensation products of other amines and amides can also be employed, for example, aldehyde condensates of triazines, diazines, diazoles, guanidines, guanimines and alkyl- and aryl-substituted derivatives of such compounds, including alkyl- and aryl-substituted melamines. Some examples of such compounds are N,N'-dimethyl urea, benzourea, dicyandiamide, formaguanamine, acetoguanamine, ammeline, 2-chloro-4,6-diamino-1,3,5-triazine, 6-methyl-2,4-diamino,1,3,5-traizine, 3,5-diaminotriazole, triaminopyrimidine,2-mercapto-4,6-diamino-pyrimidine, 3,4,6-tris(ethylamino)-1,3,5-triazine, tris(alkoxycarbonylamino)triazine, N,N,N',N'-tetramethoxymethylurea and the like.

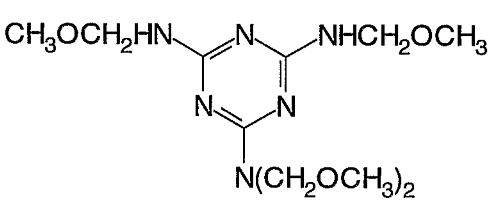
Other possible aminoplasts include compounds having the following structures:

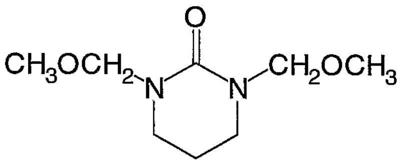


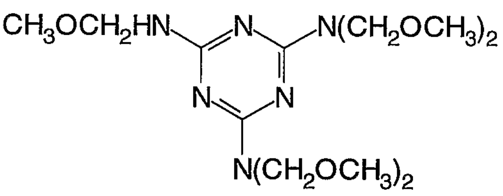






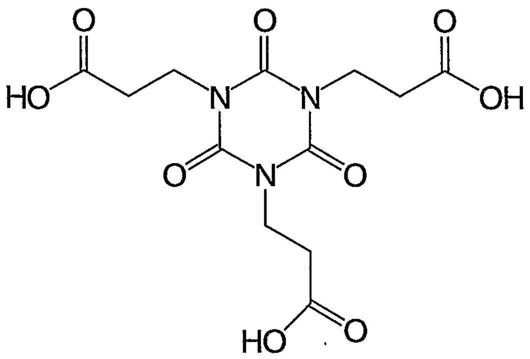


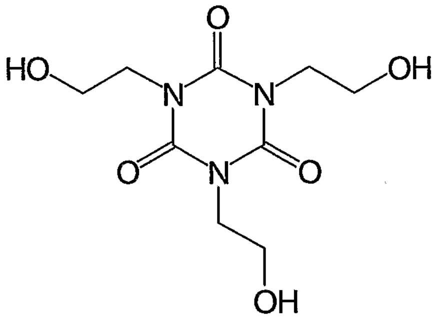




including their analogs and derivatives, such as those found in Japanese Laid-Open Patent Application (Kokai) No. 1-293339 to Tosoh, as well as etherified amino resins, for example methylated or butylated melamine resins (N-methoxymethyl- or N-butoxymethyl-melamine respectively) or methylated/butylated glycolurils, for example as can be found in Canadian Patent No. 1 204 547 to Ciba Specialty Chemicals. Various melamine and urea resins are commercially available under the Nicalacs (Sanwa Chemical Co.), Plastopal (BASF AG), or Maprenal (Clariant GmbH) tradenames. The above mentioned aminoplasts can also be used, when needed, as crosslinking agents in the present invention.

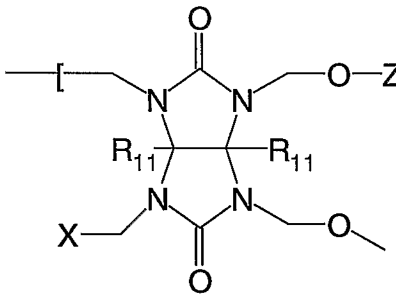
Other types of crosslinking agents include



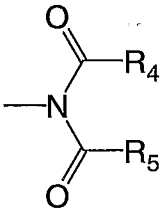


and derivatives thereof.

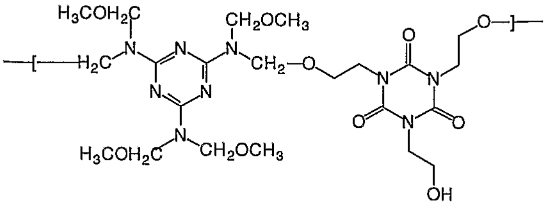
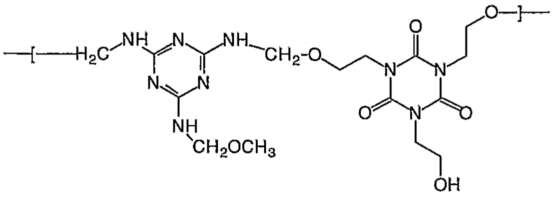
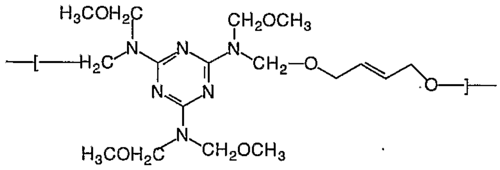
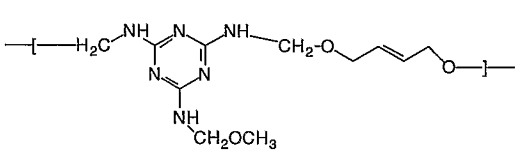
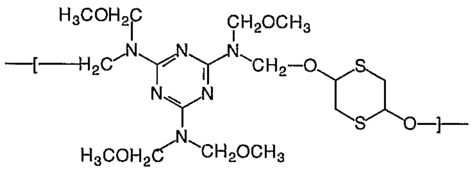
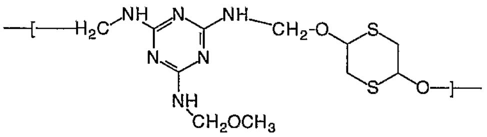
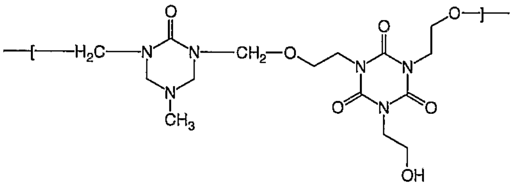
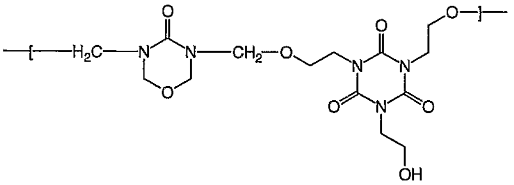
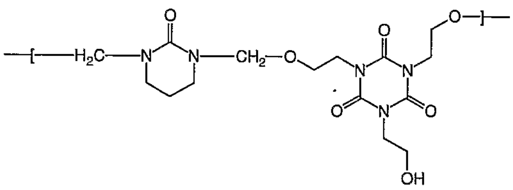
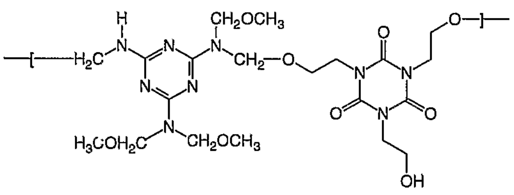
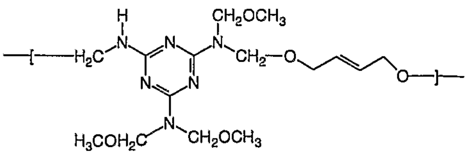
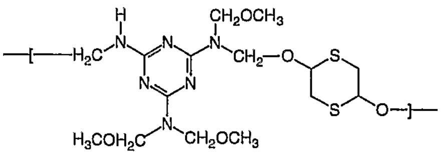
One example of a repeating unit from the polymer of the present invention is

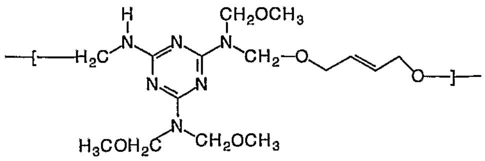


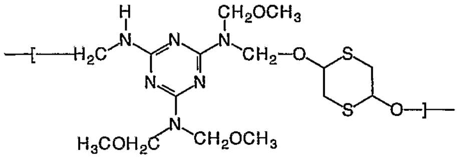
(1A)

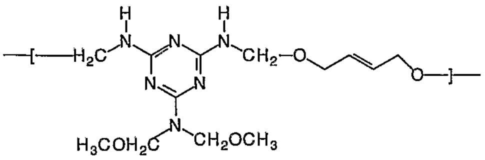
where Z is a residue of a diol, triol, dithiol, trithiol, other polyols, diacid, triacid, other polyacids, diimide, diamide, imide-amide, or mixture thereof; X is $-OR_3$, $-O(O{=}C)R_3$, or  where R_3 is hydrogen, unsubstituted or substituted alkyl, unsubstituted or substituted alkene, unsubstituted or substituted alkyne, or unsubstituted or substituted 6-membered ring optionally having one or more nitrogen and/or sulfur atoms within the ring; each of R_4 and R_5 are independently R_3 or R_4 and R_5 together with the atoms to which they are attached form an unsubstituted or substituted 5- or 6-membered ring optionally having one or more nitrogen and/or sulfur atoms within the ring; and each of R_{11} is hydrogen or C_{1-6} alkyl.

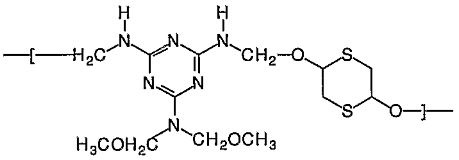
Further examples of repeating units include

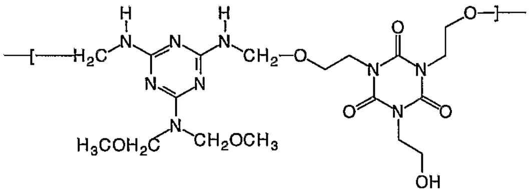













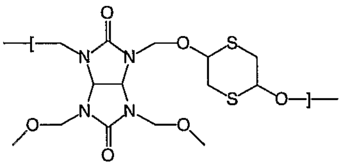


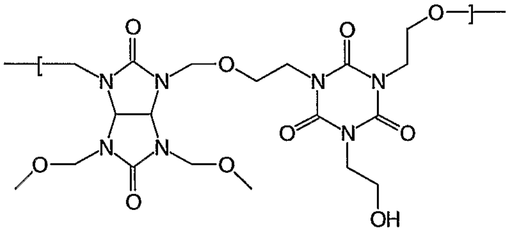


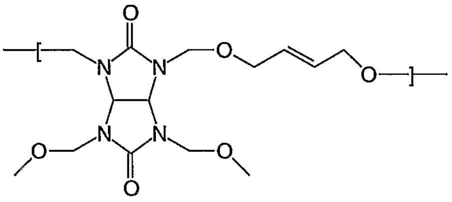


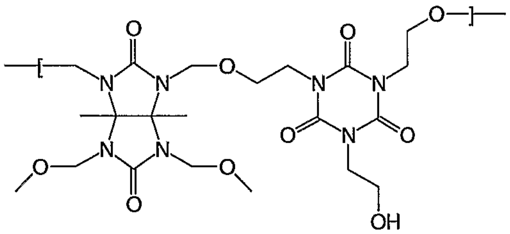


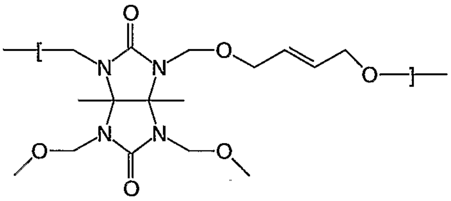


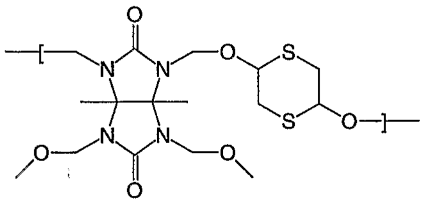


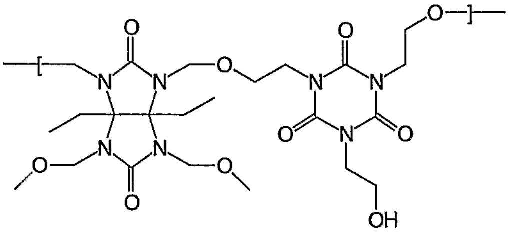


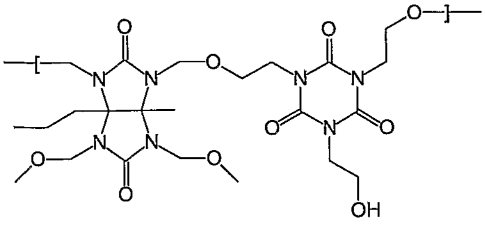


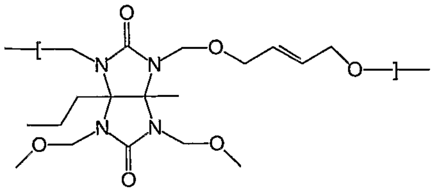


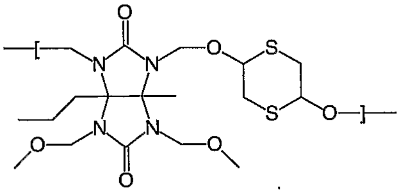


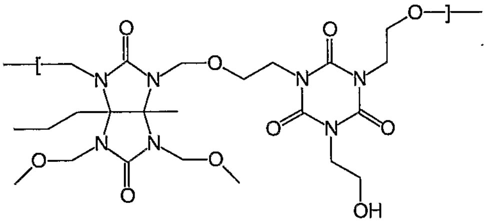


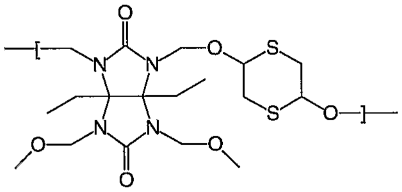


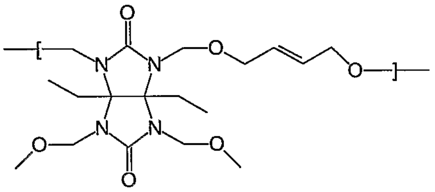


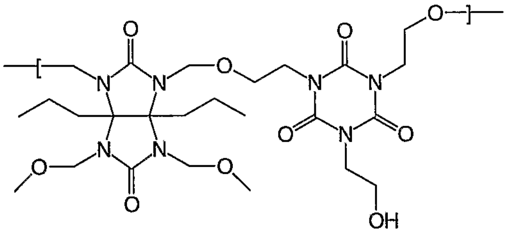


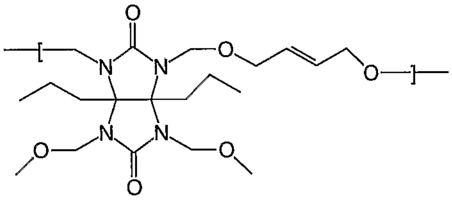


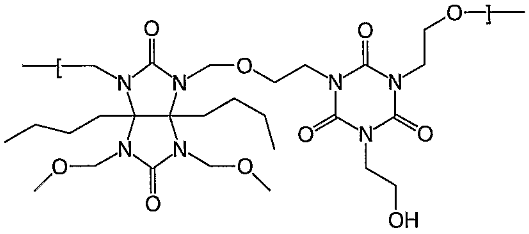


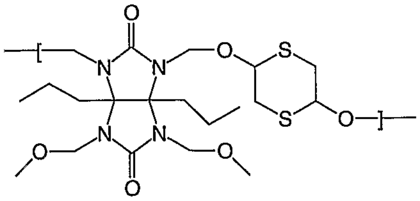


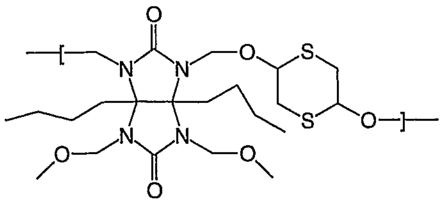


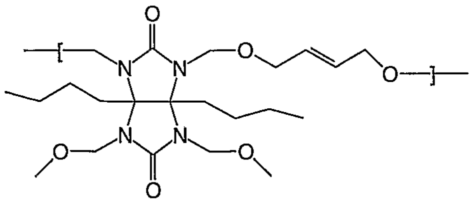


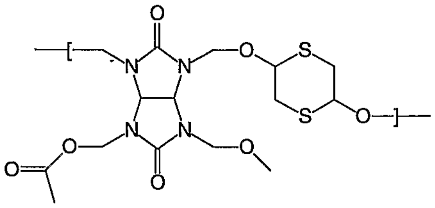


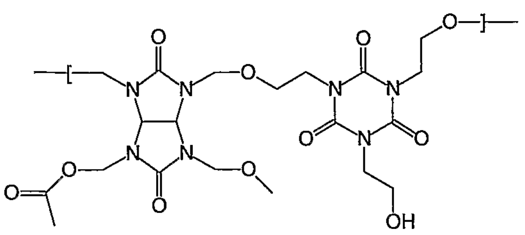


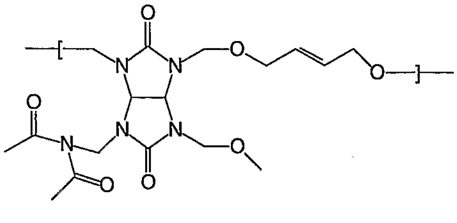


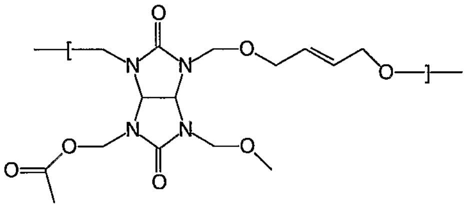


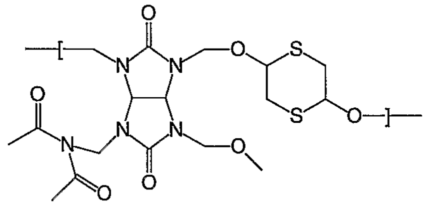


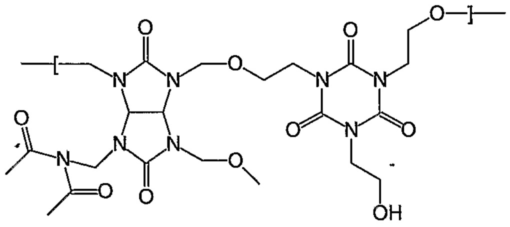


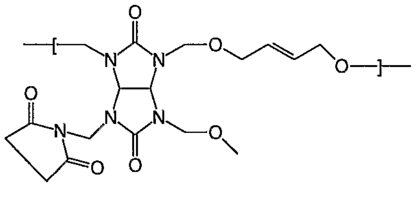


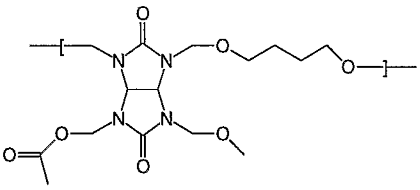


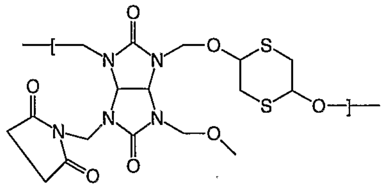


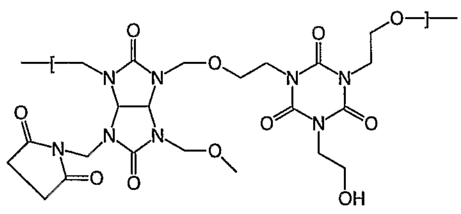


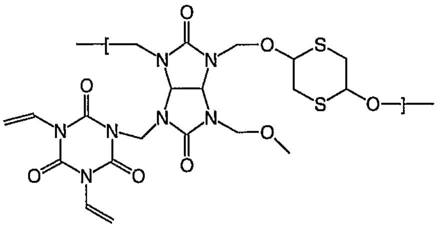


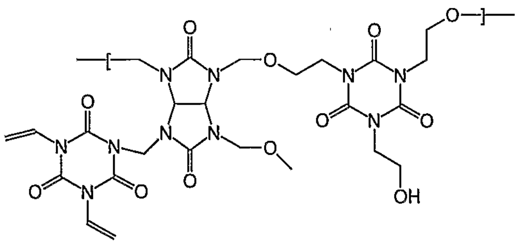


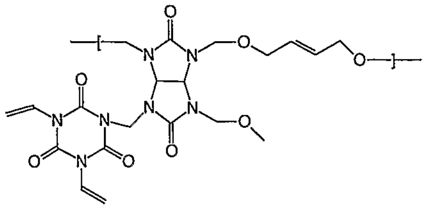


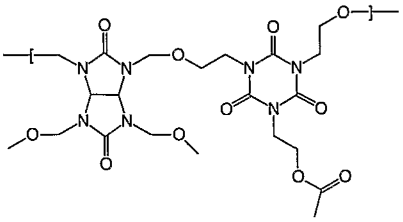


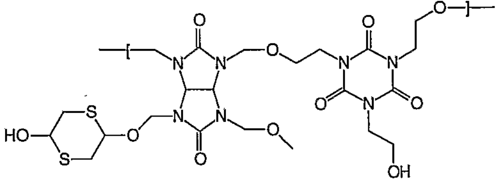


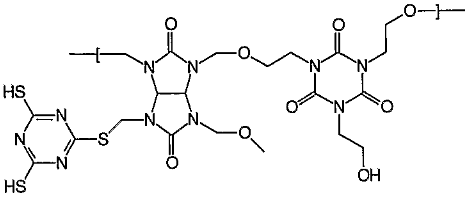


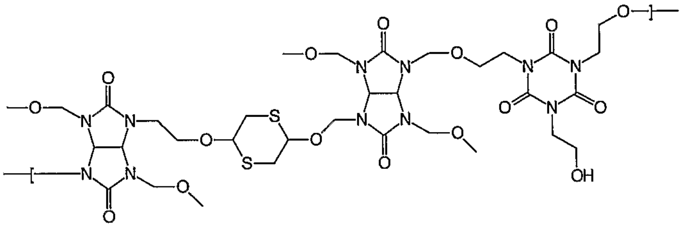


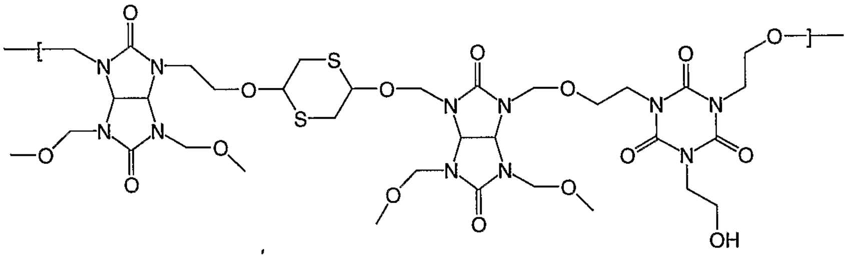


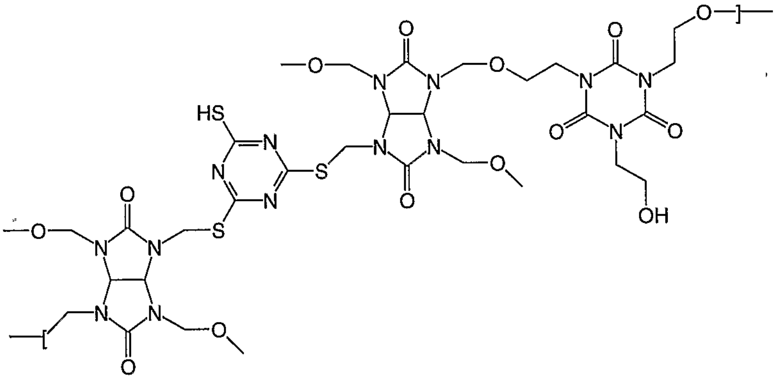


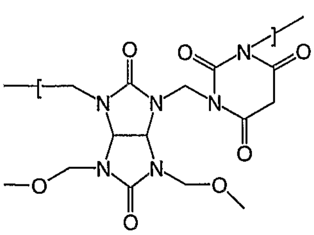


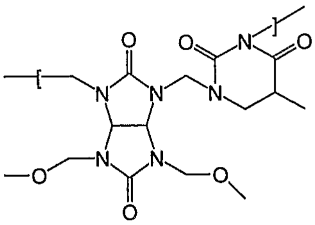


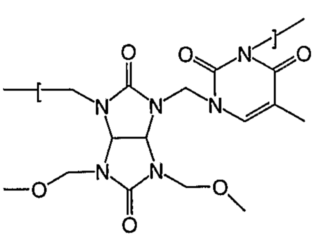


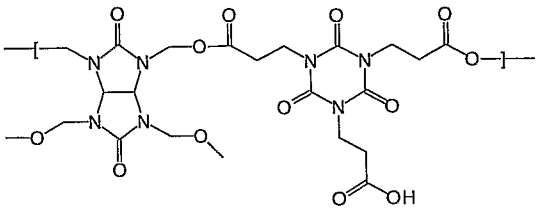


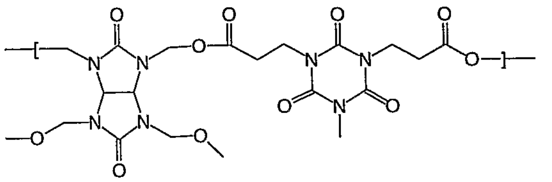


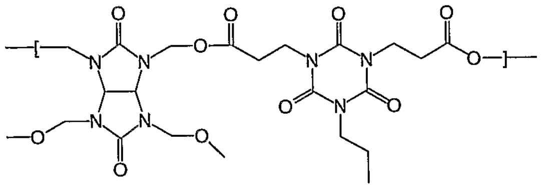


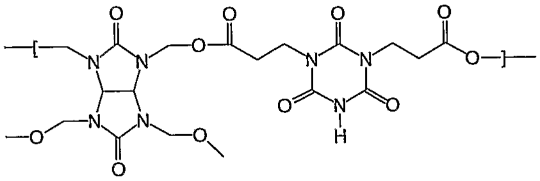


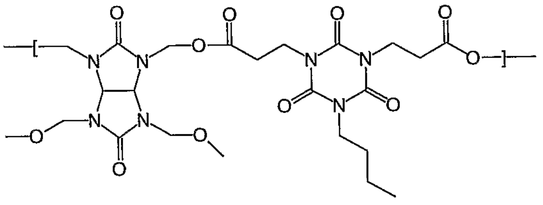


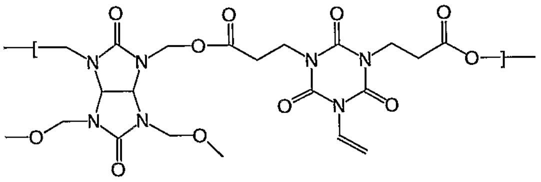












The polymers of this invention may be prepared by any of the standard polymerization methods known in the art, especially condensation polymerization techniques. The polymer may be synthesized using solution, emulsion, bulk, suspension polymerization, or the like. Typically, the aminoplast is condensed with a diol, triol, dithiol, trithiol, or a mixture thereof, at elevated temperatures, and optionally in the presence of an acid, to give the polymer of the present invention. A typical ratio of aminoplast to diol, triol, dithiol, trithiol, other polyols, diacid, triacid, other polyacids, diimide or mixtures thereof range between 1:2 to about 3:1, further from about 1:1.5 to about 2.5:1.

The acid generator used with the present invention, preferably a thermal acid generator is a compound which, when heated to temperatures greater than 90°C. and less than 250°C., generates an acid. The acid, in combination with the crosslinker, crosslinks the polymer. The antireflective coating layer after heat treatment becomes insoluble in the solvents used for coating photoresists, and furthermore, is also insoluble in the alkaline developer used to image the photoresist. Preferably, the thermal acid generator is activated at 90°C. and more preferably at above 120°C., and even more preferably at above 150°C. The antireflective coating layer is heated for a sufficient length of time to crosslink the coating. Examples of acids and thermal acid generators are butane sulfonic acid, triflic acid, nanoflurobutane sulfonic acid, nitrobenzyl tosylates, such as 2-nitrobenzyl tosylate, 2,4-dinitrobenzyl tosylate, 2,6-dinitrobenzyl tosylate, 4-nitrobenzyl tosylate; benzenesulfonates such as 2-trifluoromethyl-6-nitrobenzyl 4-chlorobenzenesulfonate, 2-trifluoromethyl-6-nitrobenzyl 4-nitro benzenesulfonate; phenolic sulfonate esters such as phenyl, 4-methoxybenzenesulfonate; alkyl ammonium salts of organic acids, such as triethylammonium salt of 10-camphorsulfonic acid, and the like.

Thermal acid generators are preferred over free acids, although free acids may also be used, in the novel antireflective composition, since it is possible that over time the shelf stability of the antireflective solution will be affected by the presence of the acid, if the polymer were to crosslink in solution. Thermal acid generators are only activated when the antireflective film is heated on the substrate. Additionally, mixtures of thermal acids and free acids may be used. Although thermal acid generators are preferred for crosslinking the polymer efficiently, an anti-reflective coating composition comprising the polymer and crosslinking agent may also be used, where heating crosslinks the polymer. Examples of a free acid are, without limitation, strong acids, such as sulfonic acids. Sulfonic acids such as toluene sulfonic acid, triflic acid or mixtures of these are preferred.

The novel composition may further contain a photoacid generator, examples of which without limitation, are onium salts, sulfonate compounds, nitrobenzyl esters, triazines, etc. The preferred photoacid generators are onium salts and sulfonate esters of hydoxyimides, specifically diphenyl iodnium salts, triphenyl sulfonium salts, dialkyl iodonium salts, triakylsulfonium salts, and mixtures thereof. One or more cross-linking catalysts can be used in the composition.

Examples of solvents for the coating composition include alcohols, esters, glymes, ethers, glycol ethers, glycol ether esters, ketones, lactones, cyclic ketones, and mixtures thereof. Examples of such solvents include, but are not limited to, propylene glycol methyl ether, propylene glycol methyl ether acetate, cyclohexanone, 2-heptanone, ethyl 3-ethoxy-propionate, propylene glycol methyl ether acetate, ethyl lactate, gamma valerolactone, methyl 3-methoxypropionate, and mixtures thereof. The solvent is typically present in an amount of from about 40 to about 99 weight percent. In certain instances, the addition of lactone solvents is useful in helping flow characteristics of the antireflective coating composition when used in layered systems. When present, the lactone solvent comprises about 1 to about 10% of the solvent system. γ-valerolactone is a useful lactone solvent.

The amount of the polymer in the present composition can vary from about 100 weight % to about 1 weight % relative to the solid portion of the composition. The amount of the crosslinker in the present composition, when used, can vary from 0 weight % to about 50 weight % relative to the solid portion of the composition. The amount of the acid generator in the present composition can vary from 0.1 weight % to about 10 weight % relative to the solid portion of the composition.

The present composition can optionally comprise additional materials typically found in antireflective coating compositions such as, for example, monomeric dyes, lower alcohols, surface leveling agents, adhesion promoters, antifoaming agents, etc, provided that the performance is not negatively impacted.

Since the composition is coated on top of the substrate and is further subjected to dry etching, it is envisioned that the composition is of sufficiently low metal ion level and purity that the properties of the semiconductor device are not adversely affected. Treatments such as passing a solution of the polymer, or compositions containing such polymers, through an ion exchange column, filtration, and extraction processes can be used to reduce the concentration of metal ions and to reduce particles.

The optical characteristics of the antireflective coating are optimized for the exposure wavelength and other desired lithographic characteristics. As an example the absorption parameter (k) of the novel composition for 193 nm exposure ranges from about 0.1 to about 1.0, preferably from about 0.2 to about 0.75, more preferably from about 0.11 to about 0.35 as measured using ellipsometry. The value of the refractive index (n) ranges from about 1.25 to about 2.0, preferably from about 1.8 to about 2.0. Due to the good absorption characteristics of this composition at 193 nm, very thin antireflective films of the order of about 20 nm may be used. This is particularly advantageous when using a nonaromatic photoresist, such as those sensitive at 193 nm, 157 nm and lower wavelengths, where the photoresist films are thin and must act as an etch mask for the antireflective film.

The substrates over which the antireflective coatings are formed can be any of those typically used in the semiconductor industry. Suitable substrates include, without limitation, silicon, silicon substrate coated with a metal surface, copper coated silicon wafer, copper, substrate coated with antireflective coating, aluminum, polymeric resins, silicon dioxide, metals, doped silicon dioxide, silicon nitride, silicon oxide nitride, titanium nitride, tantalum, tungsten, copper, polysilicon, ceramics, aluminum/copper mixtures; gallium arsenide and other such Group III/V compounds, and the like. The substrate may comprise any number of layers made from the materials described above.

The coating composition can be coated on the substrate using techniques well known to those skilled in the art, such as dipping, spincoating or spraying. The film thickness of the anti-reflective coating ranges from about 0.01 µm to about 1 µm. The coating can be heated on a hot plate or convection oven or other well known heating methods to remove any residual solvent and induce crosslinking if desired, and insolubilizing the anti-reflective coatings to prevent intermixing between the anti-reflective coating and the photoresist. The preferred range of temperature is from about 90°C to about 250°C. If the temperature is below 90°C then insufficient loss of solvent or insufficient amount of crosslinking takes place, and at temperatures above 300°C the composition may become chemically unstable. A film of photoresist is then coated on top of the uppermost antireflective coating and baked to substantially remove the photoresist solvent. An edge bead remover may be applied after the coating steps to clean the edges of the substrate using processes well known in the art.

There are two types of photoresist compositions, negative-working and positive-working. When negative-working photoresist compositions are exposed image-wise to radiation, the areas of the resist composition exposed to the radiation become less soluble to a developer solution (e.g. a cross-linking reaction occurs) while the unexposed areas of the photoresist coating remain relatively soluble to such a solution. Thus, treatment of an exposed negative-working resist with a developer causes removal of the non-exposed areas of the photoresist coating and the creation of a negative image in the coating, thereby uncovering a desired portion of the underlying substrate surface on which the photoresist composition was deposited.

On the other hand, when positive-working photoresist compositions are exposed image-wise to radiation, those areas of the photoresist composition exposed to the radiation become more soluble to the developer solution (e.g. a rearrangement reaction occurs) while those areas not exposed remain relatively insoluble to the developer solution. Thus, treatment of an exposed positive-working photoresist with the developer causes removal of the exposed areas of the coating and the creation of a positive image in the photoresist coating. Again, a desired portion of the underlying surface is uncovered.

Negative working photoresist and positive working photoresist compositions and their use are well known to those skilled in the art.

Along with the positive and negative photoresists mentioned above, which are typically done dry, 193 nm immersion lithography is a viable solution for nodes down to 45 nm node and beyond. With absorptive underlayers at 193 nm, low "k" BARCs are more suitable for optimum substrate reflectivity control based on simulations. On the other hand, the BARC film needs to be thin enough to have desired etch selectivity for very small features in thin film lithography. The low film thickness requires high n value for BARCs. This invention describes an antireflective coating composition which contains a novel polymer with non-aromatic dyes. The dye is less absorbing at 193 nm than that of conventional 193 nm BARC, e.g. phenyl or its derivatives. The invention takes advantage of anomalous dispersion effects near the absorption maxima λ_{max} (excluding λ_{max}) by a judicious choice of the dye. The dye with absorbance maxima lower than the exposure absorbance (193 nm) is used to achieve hyper n value. Theoretically, a n value that is above the value predicted from the Cauchy correlation is considered high, which covers entire half of the absorbance band in high wavelength area. When a moderately strong dye is used, the high n low k material should ideally have absorption maxima, λ_{max}, such that the actinic wavelength is the same as the wavelength λ_+ that is at half height of the absorption band on the higher wavelength side of the absorption band (Fig. 1). The absorption maxima λ_{max} moving from that position in the shorter wavelength direction up to a half length ($\lambda_{max} - \lambda_-$) forces exposure wavelength λ to fall into a typical high n low k region indicated in Fig. 1. The amplitude of the refractive index fluctuation is not only determined by the position of λ_{max} but also influenced by the strength of absorbance based on a Kramers-Kronic relation. In principle, nearly any increment of n value can be achieved as long as the dye has extremely strong absorbance corresponding to the anomalous dispersion area. The low k requirement of the organic BARC limits the amplitude of n enhancement and adds challenges in dye selection and material development. We have successfully incorporated dyes with absorption maxima between 160-190 nm, preferably between 170-190 nm such as cyanuric acid, alkene, alkyne or ketone, into the polymer structure. An example of dispersion curve based on Coating Example 2 (polymer from Synthesis Example 2) is shown in Fig. 2, measured by using ellipsometric spectroscopy. The prediction based on Cauchy correlation results in an n value of 1.63 at 193 nm assuming the material is transparent. The actual n value of the material is measured to be 1.93. Thus, a refractive index increment of 0.30 is attributed to the dispersion effect although the exposure wavelength is not exactly at the optimum high n low k position.

It should be mentioned that optical indices used in the antireflective coating is not the same as the absorption property of organic compound in its pure form or in its liquid solution. The absorption spectrum of a dye in coating may shift due to changes of chemical and physical environment such as solvent, additives and possible chemical reactions. A dye behaves ideally in solution may not be right for antireflective coating. The invention has studied many low k BARC materials with various carefully selected dyes and the structures are presented in this work.

In the present invention, the the diol, triol, dithiol, trithiol, diacid, triacid diimide, diamide, or imide-amide in the antireflective coating composition can be chosen in such a way that the absorption maximum of the polymer, in the antireflective coating composition which is used to form an antireflective film on a substrate, is less than the exposure wavelength for the photoresist and where the exposure wavelength is between the absorption maximum and the absorption minimum on the long wavelength side of the absorption band of the polymer in the antireflective coating composition, resulting in an anomalous dispersion contribution to the refractive index of the antireflective film that raises the refractive index 'n' of the antireflective film and lowers the absorption parameter 'k' of the antireflective film. In some instances, the diol, triol, dithiol, trithiol, other polyols, diacid, triacid, other polyacids, diimide, diamide, or imide-amide can be chosen such that the absorption maximum of the polymer in the antireflective coating composition is less than the exposure wavelength for the photoresist and where the exposure wavelength is between the half height of the absorption band of the polymer in the antireflective coating composition and the absorption minimum on the long wavelength side. In either instance, an anomalous dispersion contribution to the refractive index of the antireflective film results in raising the refractive index 'n' of the antireflective film and lowers the absorption parameter 'k' of the antireflective film.

A process of the instant invention comprises coating a substrate with an antireflective coating composition comprising a polymer of the present invention and heating the substrate on a hotplate or convection oven or other well known heating methods at a sufficient temperature for sufficient length of time to remove the coating solvent, and crosslink the polymer if necessary, to a sufficient extent so that the coating is not soluble in the coating solution of a photoresist or in a aqueous alkaline developer. An edge bead remover may be applied to clean the edges of the substrate using processes well known in the art. The heating ranges in temperature from about 70°C to about 250°C. If the temperature is below 70°C, then insufficient loss of solvent or insufficient amount of crosslinking may take place, and at temperatures above 250°C, the polymer may become chemically unstable. A film of a photoresist composition is then coated on top of the antireflective coating and baked to substantially remove the photoresist solvent. The photoresist is image-wise exposed and developed in an aqueous developer to remove the treated resist. An optional heating step can be incorporated into the process prior to development and after exposure. The process of coating and imaging photoresists is well known to those skilled in the art and is optimized for the specific type of resist used. The patterned substrate can then be dry etched in a suitable etch chamber to remove the exposed portions of the anti-reflective film, with the remaining photoresist acting as an etch mask. Various gases are known in the art for etching organic antireflective coatings, such as O_2, Cl_2, F_2 and CF_4 as well as other etching gases known in the art. This process is generally known as a bilayer process.

An intermediate layer may be placed between the antireflective coating and the photoresist to prevent intermixing, and is envisioned as lying within the scope of this invention. The intermediate layer is an inert polymer cast from a solvent, where examples of the polymer are polysulfones and polyimides.

In addition, a multilayer system, for example, a trilayer system, or process is also envisioned within the scope of the invention. In a trilayer process for example, an organic film is formed on a substrate, an antireflection film is formed on the organic film, and a photoresist film is formed on the antireflection film. The organic film can also act as an antireflection film. The organic film is formed on a substrate as a lower resist film by spin coating method etc. The organic film may or may not then crosslinked with heat or acid after application by spin coating method etc. On the organic film is formed the antireflection film, for example that which is disclosed herein, as an intermediate resist film. After applying the antireflection film composition to the organic film by spin-coating etc., an organic solvent is evaporated, and baking is carried out in order to promote crosslinking reaction to prevent the antireflection film from intermixing with an overlying photoresist film. After the antireflection film is formed, the photoresist film is formed thereon as an upper resist film. Spin coating method can be used for forming the photoresist film as with forming the antireflection film. After photoresist film composition is applied by spin-coating method etc., pre-baking is carried out. After that, a pattern circuit area is exposed, and post exposure baking (PEB) and development with a developer are carried out to obtain a resist pattern.

Another trilayer resist process is such when a bottom layer is formed with a carbon etch mask. On top of the bottom layer, an intermediate layer is formed by using an intermediate resist layer composition containing silicon atoms. On top of the intermediate layer, an antireflection layer based on the antireflection coating composition of the present invention, is formed. Finally, on top of the antireflection layer, a top layer is formed by using a top resist layer composition of a photoresist composition. In this case, examples of the composition for forming the intermediate layer may include polysilsesquioxane-based silicone polymer, tetraorthosilicate glass (TEOS), and the like. Then films prepared by spin-coating such a composition, or a film of SiO_2, SiN, or SiON prepared by CVD may be used as the intermediate layer. The top resist layer composition of a photoresist composition preferably comprises a polymer without a silicon atom. A top resist layer comprising a polymer without a silicon atom has an advantage of providing superior resolution to a top resist layer comprising a polymer containing silicon atoms. Then in the same fashion as the bilayer resist process mentioned above, a pattern circuit area of the top resist layer is exposed according to standard procedures. Subsequently, post exposure baking (PEB) and development are carried out to obtain a resist pattern, followed by etching and further lithographic processes.

The following examples provide detailed illustrations of the methods of producing and utilizing compositions of the present invention. These examples are not intended, however, to limit or restrict the scope of the invention in any way and should not be construed as providing conditions, parameters or values which must be utilized exclusively in order to practice the present invention.

EXAMPLES

Synthesis Example 1

32 grams of tetramethoxymethyl glycoluril, 13 grams of tris-(2-hydroxyethyl) cyanuric acid and 100 grams of cyclohexanone were charged into a 500 mL flask with a thermometer, a cold water condenser and a mechanical stirrer. The reaction mixture was heated to 80°C. After a catalytic amount of para-toluenesulfonic acid monohydrate (0.14 g) was added, the reaction was maintained at this temperature for 6.0 hours. The reaction solution was then cooled to room temperature and a ~ 30 solid% polymer solution was obtained. The average molecular weight of the polymer is about 2000 g/mol.

Synthesis Example 2

29 grams of tetramethoxymethyl glycoluril, 16 grams of tris-(2-hydroxyethyl) cyanuric acid and 100 grams of cyclohexanone were charged into a 500 mL flask with a thermometer, a cold water condenser and a mechanical stirrer. The reaction mixture was heated to 80°C. After a catalytic amount of para-toluenesulfonic acid monohydrate (0.14 g) was added, the reaction was maintained at this temperature for 6.0 hours. The reaction solution was then cooled to room temperature and a ~ 30 solid% polymer solution was obtained. The average molecular weight of the polymer is about 2000 g/mol.

Synthesis Example 3

6.1 g acetic anhydride, 13 grams of tris-(2-hydroxyethyl) cyanuric acid and 120 grams of cyclohexanone were charged into a 500 mL flask with a thermometer, a cold water condenser and a mechanical stirrer. The mixture was heated to 100°C and 0.11 g of para-toluenesulfonic acid monohydrate was added. After 16 h, the reaction mixture was cooled to 80°C and 32 grams of tetramethoxymethyl glycoluril was added. The reaction was maintained at this temperature for 16.0 hours. The reaction solution was then cooled to room temperature and a polymer solution was obtained.

Synthesis Example 4

32 grams of tetramethoxymethyl glycoluril, 13 grams of tris-(2-hydroxyethyl) cyanuric acid, 1.9 g of 1,4-dithiane-2,5-diol and 100 grams of cyclohexanone were charged into a 500 mL flask with a thermometer, a cold water condenser and a mechanical stirrer. The reaction mixture was heated to 80°C. After a catalytic amount of para-toluenesulfonic acid monohydrate (0.15 g) was added, the reaction was maintained at this temperature for 6.0 hours. The reaction solution was then cooled to room temperature and a ~ 30 solid% polymer solution was obtained.

Synthesis Example 5

29.2 grams of tetramethoxymethyl glycoluril, 8 grams of tris-(2-hydroxyethyl) cyanuric acid, 5.4 g of trithiocyanuric acid and 100 grams of cyclohexanone were charged into a 500 mL flask with a thermometer, a cold water condenser and a mechanical stirrer. The reaction mixture was heated to 80°C. After a catalytic amount of para-toluenesulfonic acid monohydrate (0.15 g) was added, the reaction was maintained at this temperature for 6.0 hours. The reaction solution was then cooled to room temperature and a ~ 30 solid% polymer solution was obtained.

Synthesis Example 6

29.2 grams of tetramethoxymethyl glycoluril, 16 grams of tris-(2-hydroxyethyl) cyanuric acid, 9.6 g of Isocyanuric acid diallyl ester and 100 grams of cyclohexanone were charged into a 500 mL flask with a thermometer, a cold water condenser and a mechanical stirrer. The reaction mixture was heated to 80°C. After a catalytic amount of para-toluenesulfonic acid monohydrate (0.15 g) was added, the reaction was maintained at this temperature for 6.0 hours. The reaction solution was then cooled to room temperature and a ~ 35 solid% polymer solution was obtained.

Synthesis Example A

600 grams of tetramethoxymethyl glycoluril, 96 grams of styrene glycol and 1200 grams of propylene glycol monomethyl ether acetate (PGMEA) were charged into a 2L jacketed flask with a thermometer, mechanical stirrer and a cold water condenser and heated to 85°C. After a catalytic amount of para-toluenesulfonic acid monohydrate was added, the reaction was maintained at this temperature for 5 hrs. The reaction solution was then cooled to room temperature and filtered. The filtrate was slowly poured into distilled water while stirring to precipitate the polymer. The polymer was filtered, washed thoroughly with water and dried in a vacuum oven (250 grams were obtained). The polymer obtained had a weight average molecular weight of about 17,345 g/mol and a polydispersity of 2.7.

Synthesis Example B

20 g of butanetetracarboxylic acid dianhydride, 20 g of (+)-dimethyl L-tartrate, 1.0 g of benzyltributylammonium chloride, and 70 g of PGMEA were charged into a flask with a condenser, thermal controller and a mechanical stirrer. Under nitrogen and stirring, the mixture was heated to 110°C. A clear solution was obtained after ~1-2 hr. The temperature was kept at 110°C for 4 hrs. After cooling to 60°C, 40 g of PGMEA, 60 g of acetonitrile, 68 g of propylene oxide and 30 g of tris(2,3-epoxypropyl) isocyanurate were mixed with the above solution. The reaction was kept at 52°C for 40 hrs. The reaction solution was cooled to room temperature and slowly poured into large amount of water in a high speed blender. The polymer was collected and washed thoroughly with water. Finally

the polymer was dried in a vacuum oven. 40 g of polymer was obtained with a weight average molecular weight (MW) of about 32000 g/mol.

Coating Formulation Example 1

1.0 g of polymer solution from Synthesis Example 1 was dissolved in 7 g of propylene glycol monomethyl ether acetate/propylene glycol monomethyl ether (PGMEA/PGME) 70/30 solvent to make a ~4 wt% solution. The mixture then was filtered through a micro filter with a pore size of 0.2 µm and coated on a silicon wafer and baked at 200°C for 90 seconds. The wafer was submitted for evaluation of optical parameters using a spectroscopic Ellipsometer. The optimized refractive index "n" at 193 nm and the absorption parameter "k" are listed in Table 1.

Coating Formulation Example 2

1.0 g of polymer solution from Synthesis Example 2 was dissolved in 7 g of PGMEA/PGME 70/30 solvent to make a ~4 wt% solution. The mixture then was filtered through a micro filter with a pore size of 0.2 µm and coated on a silicon wafer and baked at 200°C for 90 seconds. The wafer was submitted for evaluation of optical parameters using a spectroscopic Ellipsometer. The optimized refractive index "n" at 193 nm and the absorption parameter "k" are listed in Table 1.

Coating Formulation Example 3

1.0 g of polymer solution from Synthesis Example 3 was dissolved in 7 g of PGMEA/PGME 70/30 solvent to make a ~4 wt% solution. The mixture then was filtered through a micro filter with a pore size of 0.2 µm and coated on a silicon wafer and baked at 200°C for 90 seconds. The wafer was submitted for evaluation of optical parameters using a spectroscopic Ellipsometer. The optimized refractive index “n” at 193 nm and the absorption parameter “k” are listed in Table 1.

Coating Formulation Example 4

1.0 g of polymer solution from Synthesis Example 4 was dissolved in 7 g of PGMEA/PGME 70/30 solvent to make a ~4 wt% solution. The mixture then was filtered through a micro filter with a pore size of 0.2 µm and coated on a silicon wafer and baked at 200°C for 90 seconds. The wafer was submitted for evaluation of optical parameters using a spectroscopic Ellipsometer. The optimized refractive index “n” at 193 nm and the absorption parameter “k” are listed in Table 1.

Coating Formulation Example 5

1.0 g of polymer solution from Synthesis Example 5 was dissolved in 7 g of PGMEA/PGME 70/30 solvent to make a ~4 wt% solution. The mixture then was filtered through a micro filter with a pore size of 0.2 µm and coated on a silicon wafer and baked at 200°C for 90 seconds. The wafer was submitted for evaluation of optical parameters using a spectroscopic Ellipsometer. The optimized refractive index “n” at 193 nm and the absorption parameter “k” are listed in Table 1.

Coating Formulation Example 6

1.0 g of polymer solution from Synthesis Example 6 was dissolved in 7 g of PGMEA/PGME 70/30 solvent to make a ~4 wt% solution. The mixture then was filtered through a micro filter with a pore size of 0.2 µm and coated on a silicon wafer and baked at 200°C for 90 seconds. The wafer was submitted for evaluation of optical parameters using a spectroscopic Ellipsometer. The optimized refractive index "n" at 193 nm and the absorption parameter "k" are listed in Table 1.

Optical parameter evaluation from coating formulation examples 1 to 6 (n & k measurements at 193 nm).

Table 1

Coating Formulation Example	n	k
1	1.92	0.25
2	1.93	0.27
3	1.88	0.20
4	1.91	0.25
5	1.87	0.24
6	1.94	0.25

Litho Formulation Example 1

2.2 g of the polymer solution from Synthesis Example 1 and 0.35 g of the polymer solid from Synthesis Example A was dissolved in 80 g of PGMEA/PGME (70/30) solvent to make a 1.2 wt% solution. 0.35% of dodecylbenzene sullfonic acid /triethylamine and 1% of triphenylsulfonium nonafluorobutane sulfate was added in the polymer solution. The mixture then was filtered through a micro filter with a pore size of 0.2 μm.

Litho performance evaluation of Litho Formulation Example 1

The performance of the anti-reflective coating formulation from Litho Formulation Example 1 was evaluated using AZ® T83472 photoresist (product of AZ Electronic Materials USA Corp., Somerville, NJ). A silicon wafer was coated with AZ® 1C5D bottom antireflective coating composition (AZ Electronic Materials USA Corp., Somerville, NJ) to form a 60 nm thick film. Then a 21 nm thick film of Litho Formulation Example 1 was coated over and baked at 200°C for 90 seconds. Then a 190 nm thick film of T83472 photoresist solution was then coated over and baked at 115°C for 60 seconds. The wafer was then imagewise exposed using a Nikon NSR-306D 193 nm scanner with 0.85 NA, under dipole Y illumination of 0.9 sigma with PSM mask. The exposed wafer was baked at 110°C for 60 seconds and developed in AZ® 300 MIF developer (available from AZ Electronic Materials USA Corp., Somerville, NJ) for 30 seconds. The cleaned wafer was then examined under a scanning electron microscope. Line and space patterns showed no standing waves, no footing and no scumming, indicating efficacy of the bottom anti-reflective coating.

Litho Formulation Example 2

2.0 g of the polymer solution from Synthesis Example 1 and 0.3 g of the polymer solid from Synthesis Example B was dissolved in 3 g of γ-valerolactone and 60 g of PGMEA/PGME 30/70 solvent to make a 1.4 wt% solution. 1% dodecylbenzene sulfonic acid /triethylamine was added in the polymer solution. The mixture then was filtered through a micro filter with a pore size of 0.2 um.

Litho performance evaluation of Litho Formulation Example 2

The performance of the anti-reflective coating formulation from Litho Formulation Example 2 was evaluated using T83472 photoresist (product of AZ Electronic Materials USA Corp., Somerville, NJ). A silicon wafer was coated with AZ® 1C5D bottom antireflective coating composition (AZ Electronic Materials USA Corp., Somerville, NJ) and baked at 200°C for 90 seconds to form a 52 nm thick film. Then a 23 nm thick film of Litho Formulation Example 1 was coated over. Then a 190 nm thick T83472 photoresist solution was coated and baked at 115°C for 60 seconds. The wafer was then imagewise exposed using a Nikon NSR-306D 193 nm scanner with 0.85 NA, under dipole Y illumination of 0.9 sigma with PSM mask. The exposed wafer was baked at 110°C for 60 seconds and developed in AZ® 300 MIF developer (available from AZ Electronic Materials USA Corp., Somerville, NJ) for 30 seconds. The cleaned wafer was then examined under scanning electron microscope. Line and space patterns showed no standing waves, no footing and no scumming, indicating efficacy of the bottom anti-reflective coating.

Litho Formulation Example 3

4.4 g of the polymer solution from Synthesis Example 2 was dissolved in 5 g of γ-valerolactone and 95 g of PGMEA/PGME 30/70 solvent to make a 1.2 wt% solution. 1% of triphenylsulfonium nonafluorobutane sulfate was added in the polymer solution. The mixture then was filtered through a micro filter with a pore size of 0.2 um.

Litho performance evaluation of Litho Formulation Example 3

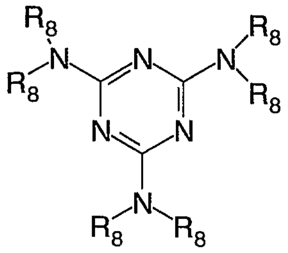
The performance of the anti-reflective coating formulation from Litho Formulation Example 3 was evaluated using T83472 photoresist (product of AZ Electronic Materials USA Corp., Somerville, NJ). A silicon wafer was coated with AZ® 1C5D bottom antireflective coating composition (AZ Electronic Materials USA Corp., Somerville, NJ) and baked at 200°C for 90 seconds to form a 60 nm thick film. Then a 20 nm thick film of Litho Formulation Example 3 was coated over. Then a 190 nm thick T83472 photoresist solution was coated and baked at 115°C for 60 seconds. The wafer was then imagewise exposed using a Nikon NSR-306D 193 nm scanner with 0.85 NA, under dipole Y illumination of 0.9 sigma with PSM mask. The exposed wafer was baked at 110°C for 60 seconds and developed in AZ® 300 MIF developer (available from AZ Electronic Materials USA Corp., Somerville, NJ) for 30 seconds. The cleaned wafer was then examined under scanning electron microscope. Line and space patterns showed no standing waves, no footing and no scumming, indicating efficacy of the bottom anti-reflective coating.

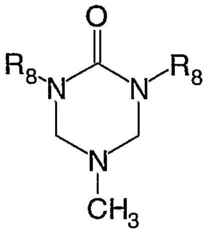
The foregoing description of the invention illustrates and describes the present invention. Additionally, the disclosure shows and describes only the preferred embodiments of the invention but, as mentioned above, it is to be understood that the invention is capable of use in various other combinations, modifications, and environments and is capable of changes or modifications within the scope of the inventive concept as expressed herein, commensurate with the above teachings and/or the skill or knowledge of the relevant art. The embodiments described hereinabove are further intended to explain best modes known of practicing the invention and to enable others skilled in the art to utilize the invention in such, or other, embodiments and with the various modifications required by the particular applications or uses of the invention. Accordingly, the description is not intended to limit the invention to the form disclosed herein. Also, it is intended that the appended claims be construed to include alternative embodiments.

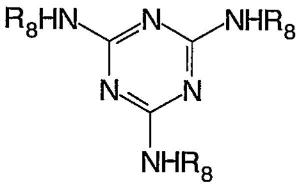
Claims:

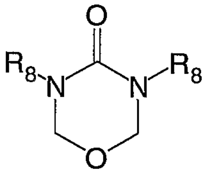
1. An antireflective coating composition comprising a polymer which does not contain an aromatic chromophore, an acid generator, and optionally a crosslinking agent, where the polymer comprises a structural unit derived from an aminoplast and a structural unit derived from a diol, triol, dithiol, trithiol, other polyols, diacid, triacid, other polyacids, diimide, diamide, imide-amide, or mixture thereof, where the diol, dithiol, triol, trithiol, diacid, triacid, diimide, diamide, or imide-amide optionally contain one or more nitrogen and/or sulfur atoms or contain one or more alkene groups.

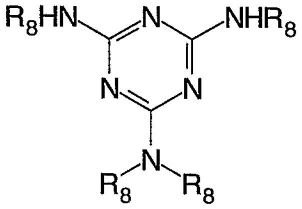
2. The antireflective coating composition of claim 1 where the aminoplast is selected from

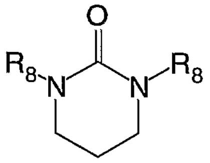


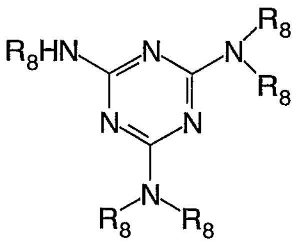


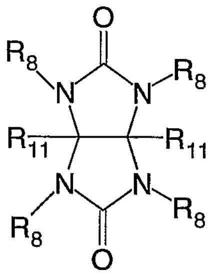




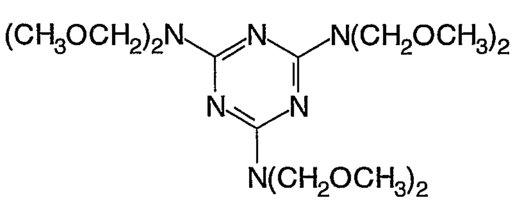


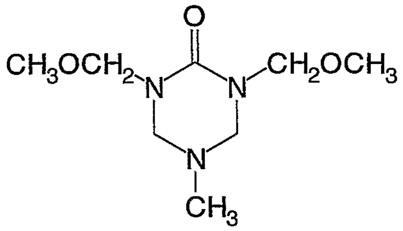


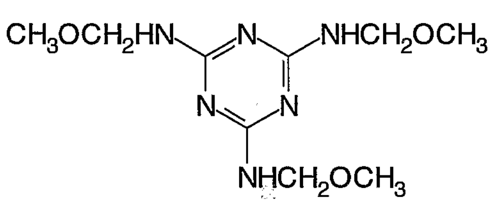


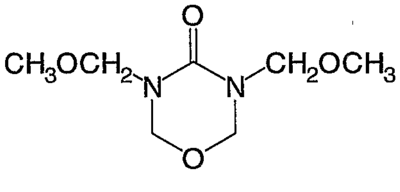


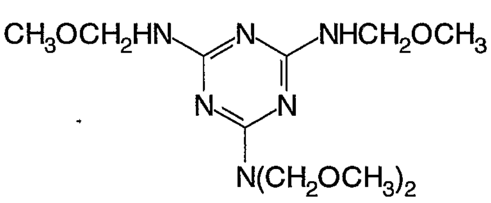
where each R_8 is $(CH_2)_n-O-(CH_2)_m-CH_3$, each R_{11} is hydrogen or C_1-C_6 alkyl, n is 1 to 4, and m is 0 to 3,

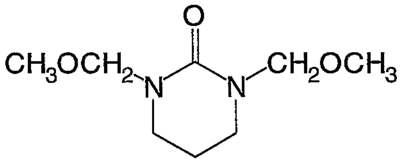


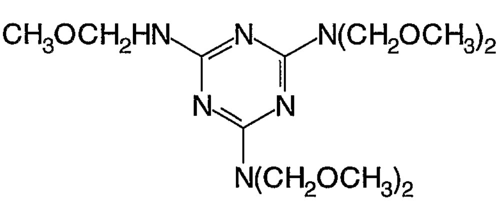


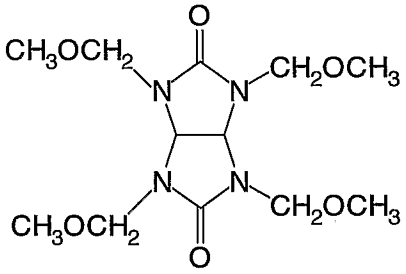


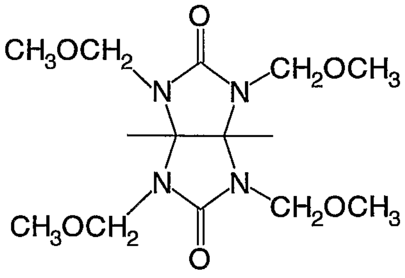


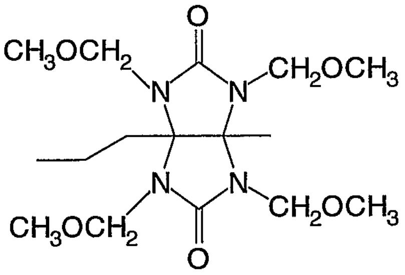


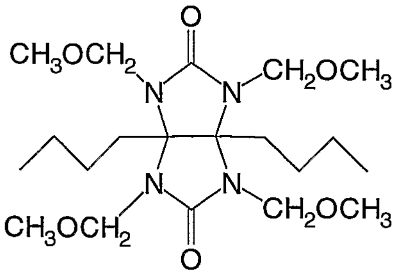








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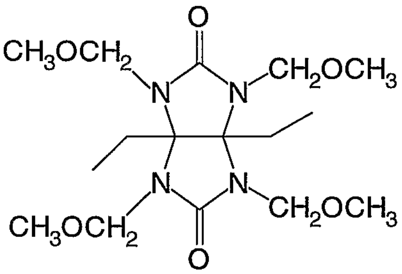
N
N
CH2OCH3
N
N
CH3OCH2
CH2OCH3
O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N
CH2OCH3
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N
CH3OCH2
CH2OCH3
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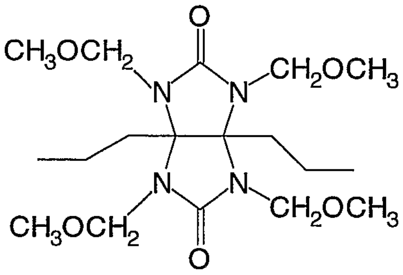
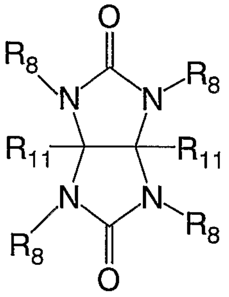
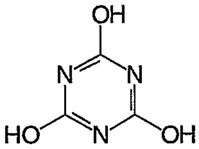

O
CH3OCH2
N
N
CH2OCH3
N
N
CH3OCH2
CH2OCH3
O

or where the aminoplast is


O
R8
N
N
R8
R11
R11
N
N
R8
R8
O

where each R_8 is $(CH_2)_n{-}O{-}(CH_2)_m{-}CH_3$, each R_{11} is hydrogen or C_1-C_6 alkyl, n is 1 to 4, and m is 0 to 3.

3. The antireflective coating composition of claim 1 or 2 where the diol, dithiol, triol, trithiol, diacid, triacid, diimide, diamide, or imide-amide are selected from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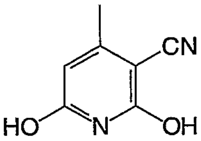
OH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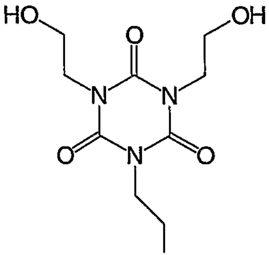
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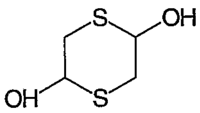
N
O
OH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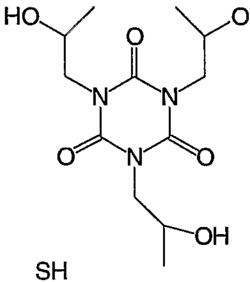
OH
OH
S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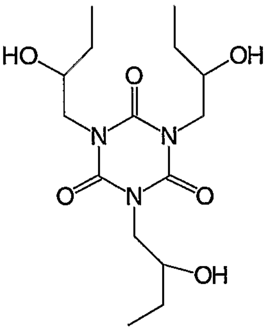
O
N
O
OH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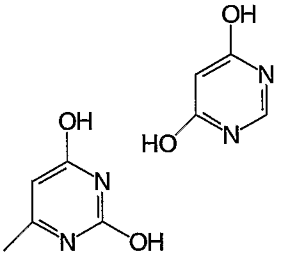
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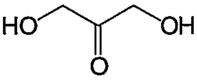
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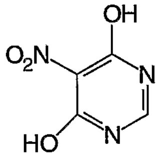
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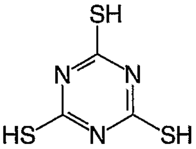
N
HO
N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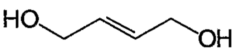
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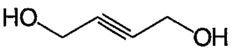
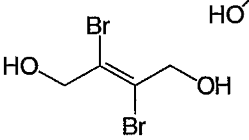
OH


HO
OH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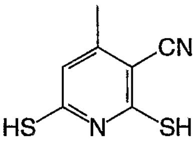
HO
OH
Br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HS
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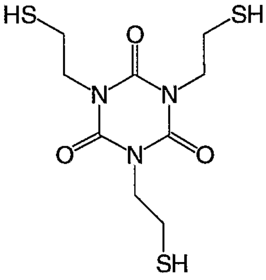
SH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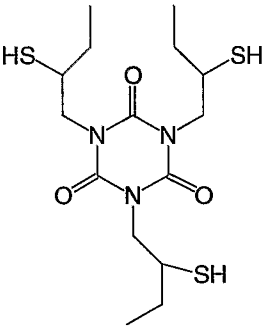
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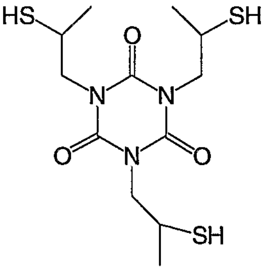
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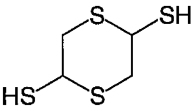
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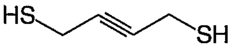
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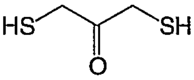
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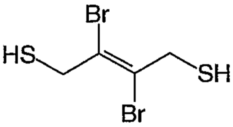
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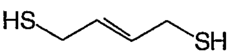
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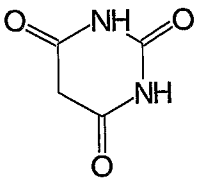
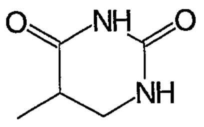
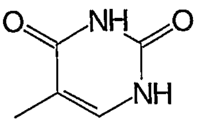
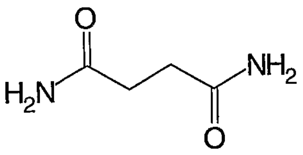
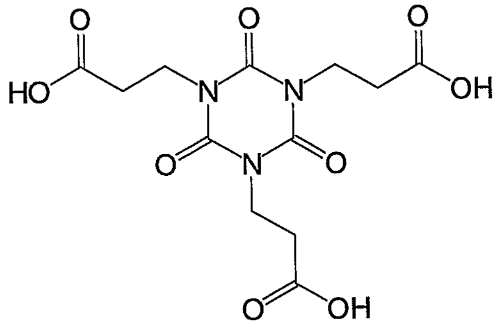
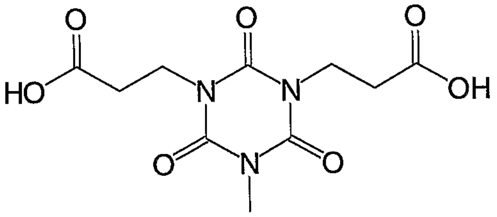


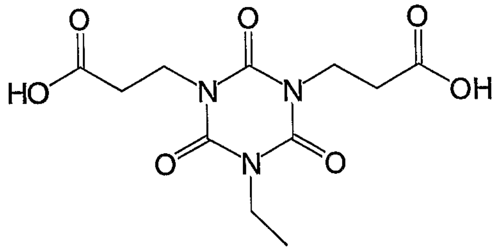


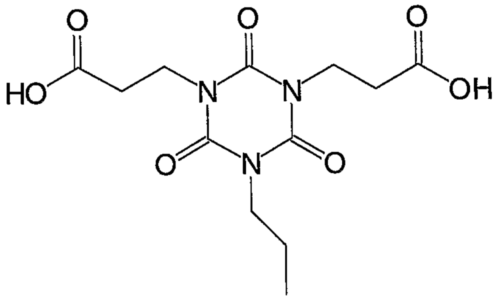


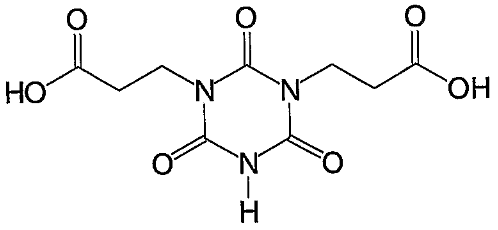


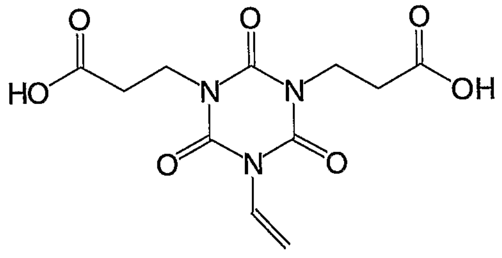




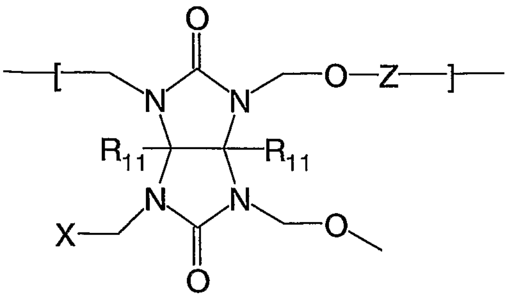






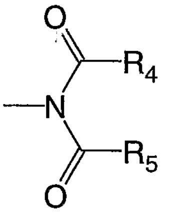


4. The antireflective coating composition of any one of claims 1 to 3 wherein the polymer comprises a repetitive unit of structure (1A)



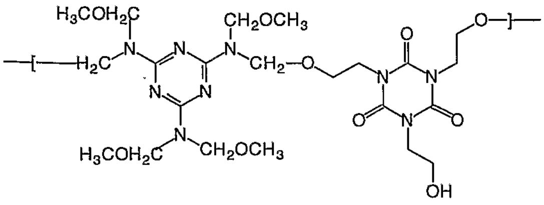
(1A)

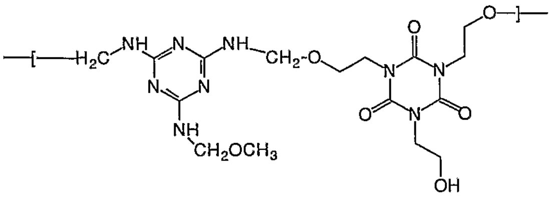
where Z is a residue of a diol, triol, dithiol, trithiol, other polyols, diacid, triacid, other polyacids, diimide, diamide, imide-amide, or mixture thereof; X is $-OR_3$, $-O(O{=}C)R_3$, or

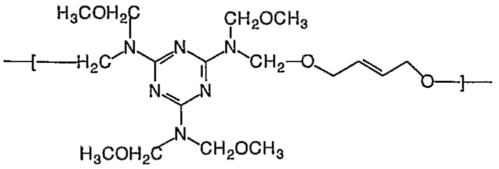


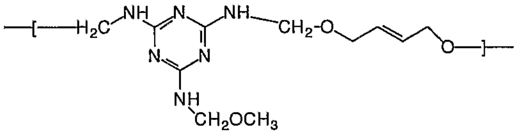
where R_3 is hydrogen, unsubstituted or substituted alkyl, unsubstituted or substituted alkene, unsubstituted or substituted alkyne, or unsubstituted or substituted 6-membered ring optionally having one or more nitrogen and/or sulfur atoms within the ring; each of R_4 and R_5 are independently R_3 or R_4 and R_5 together with the atoms to which they are attached form an unsubstituted or substituted 5- or 6-membered ring optionally having one or more nitrogen and/or sulfur atoms within the ring; and each of R_{11} is hydrogen or C_{1-6} alkyl,

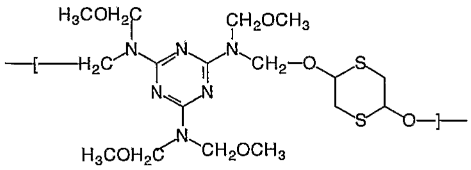
or a repetitive unit selected from

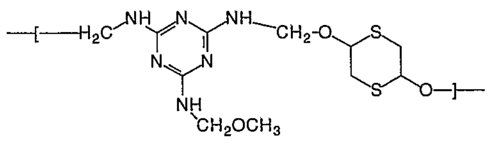


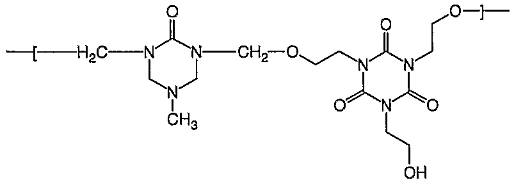


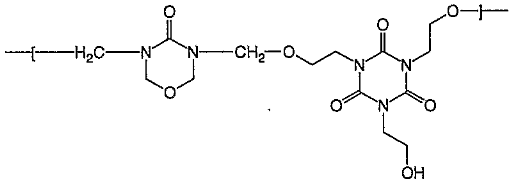


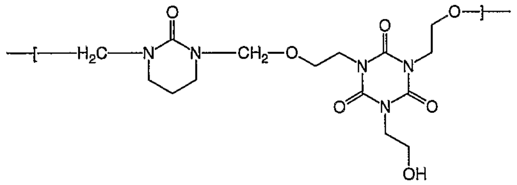


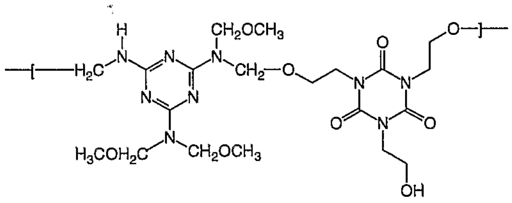


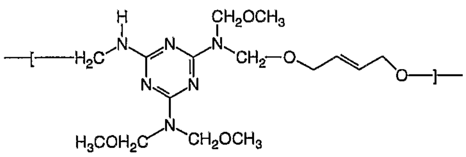


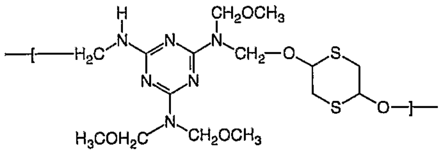


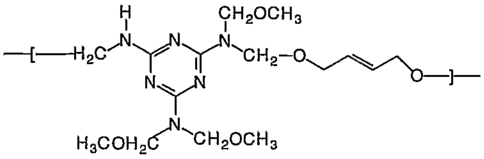


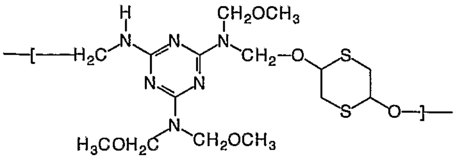


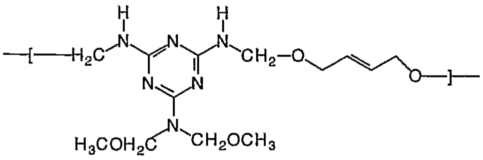


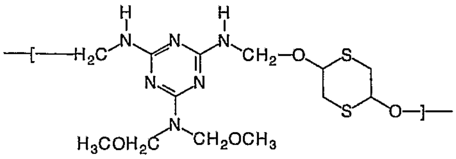


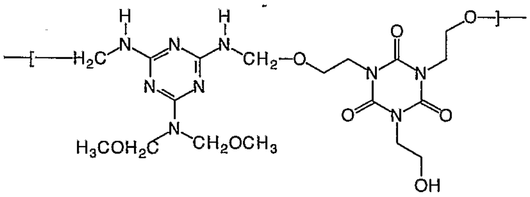


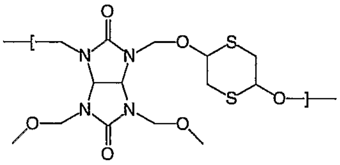


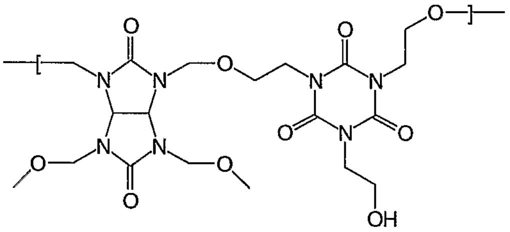


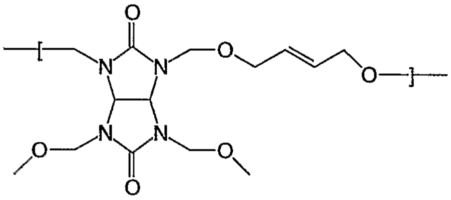


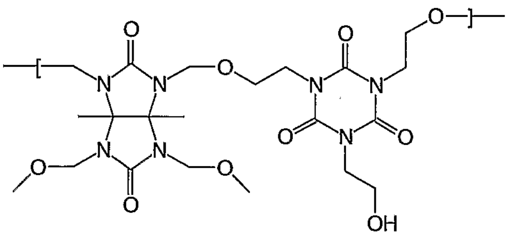


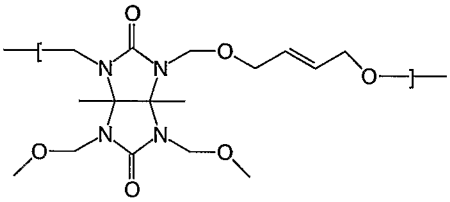


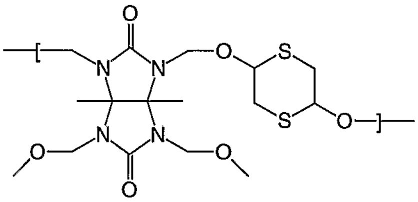


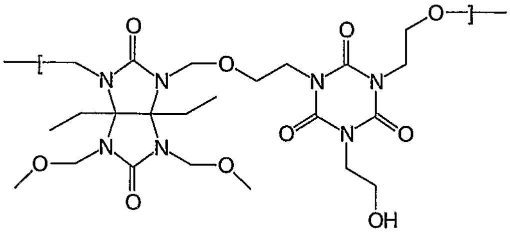


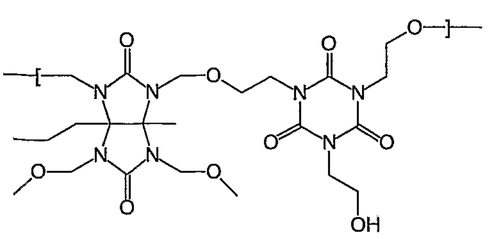


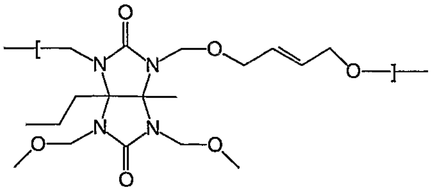


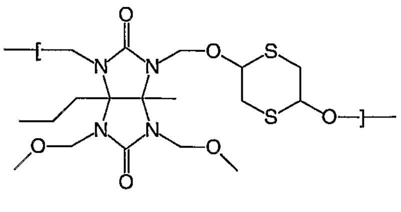


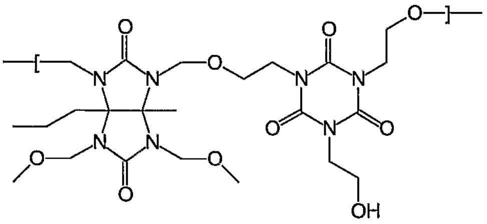


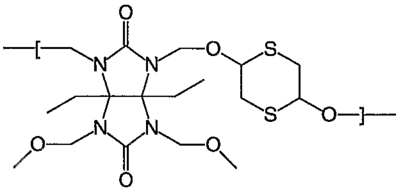


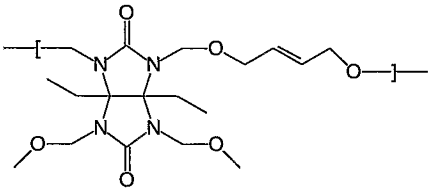


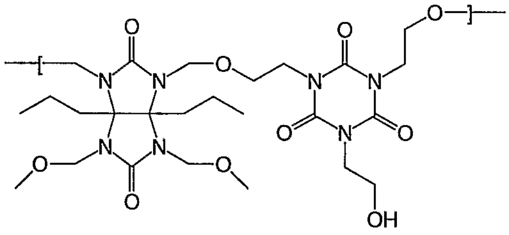


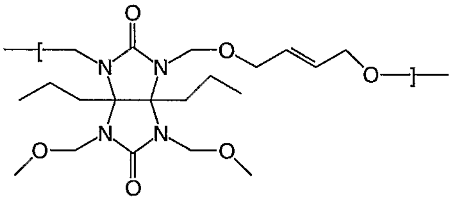


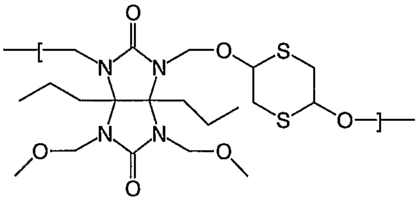


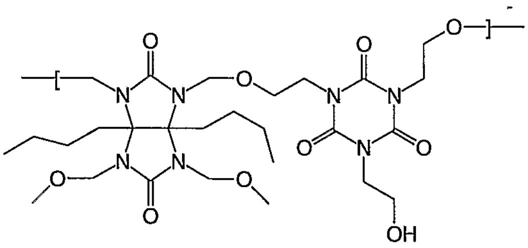


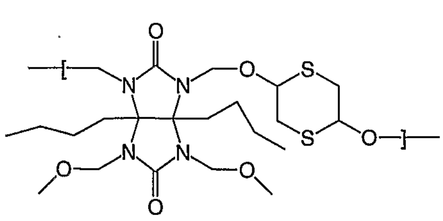


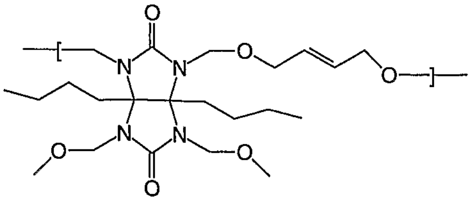


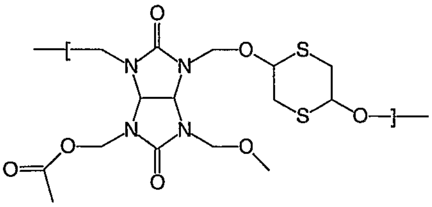


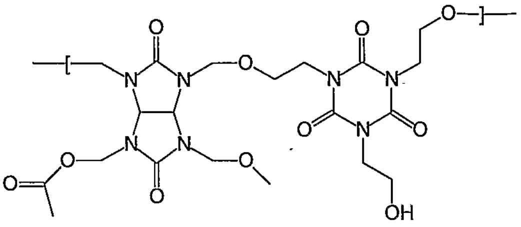


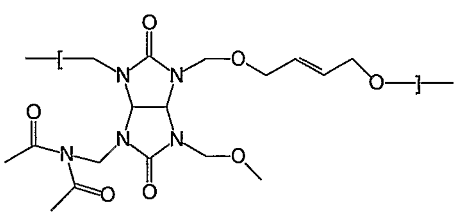


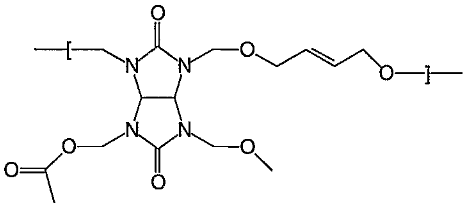


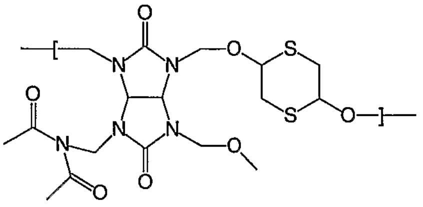


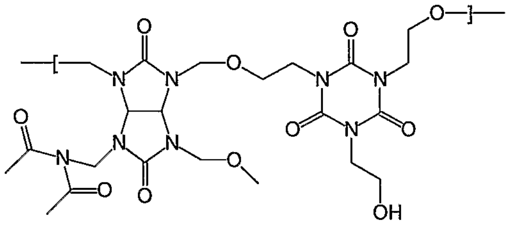


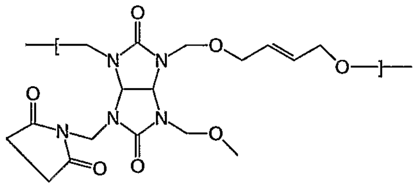


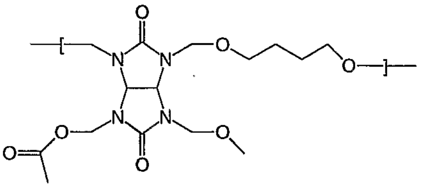


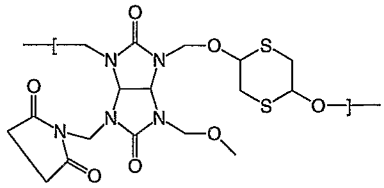


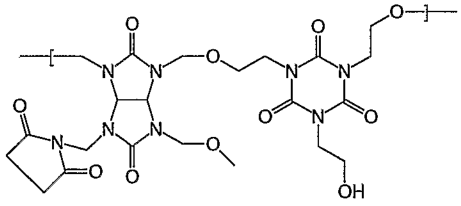


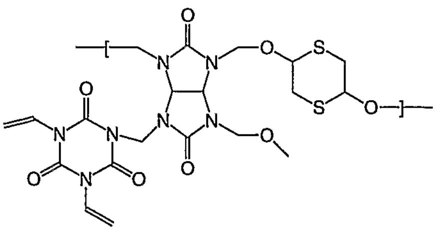


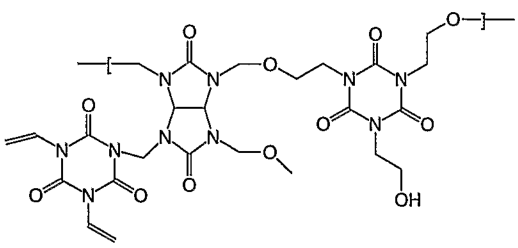


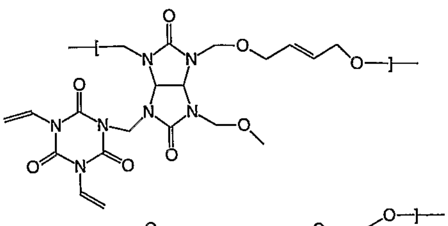


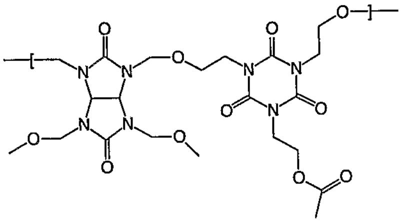


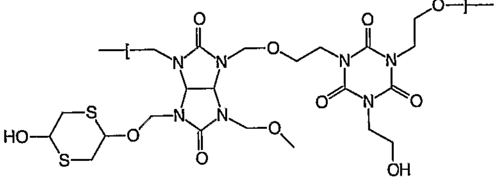


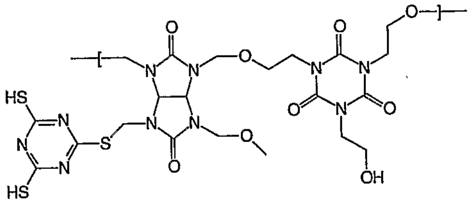


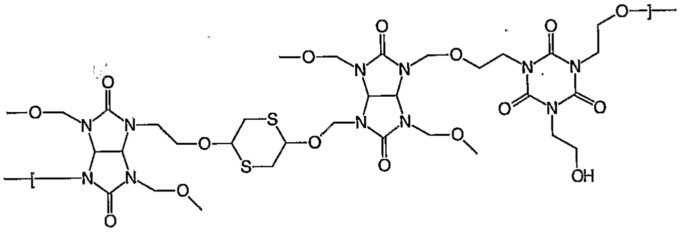


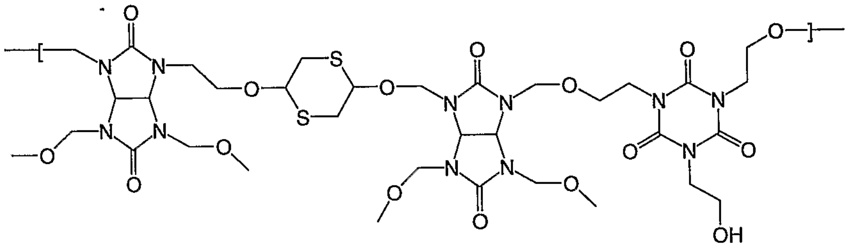


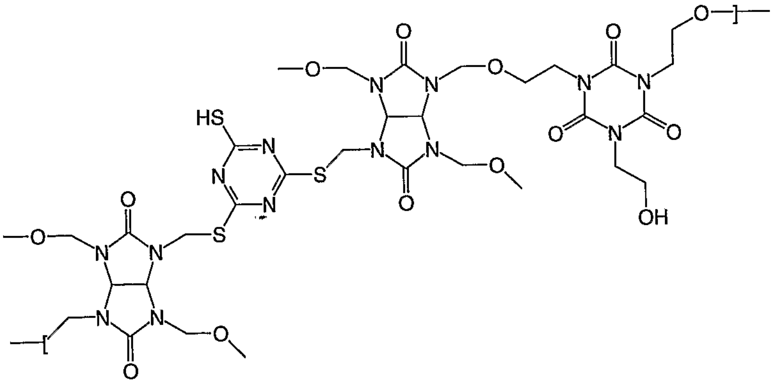


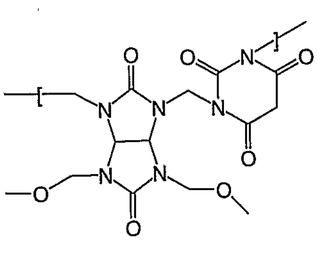


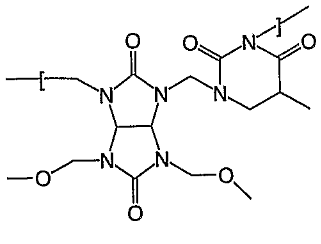


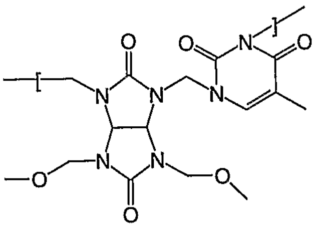


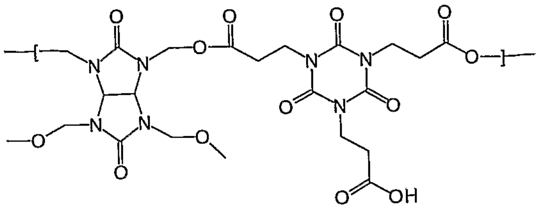


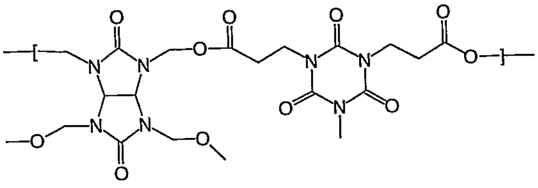


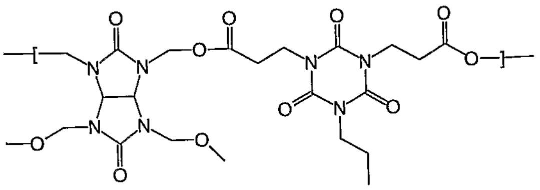


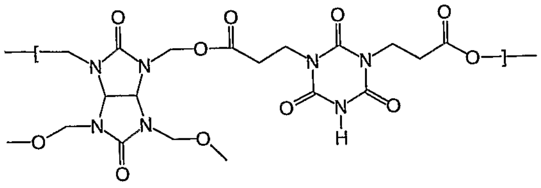


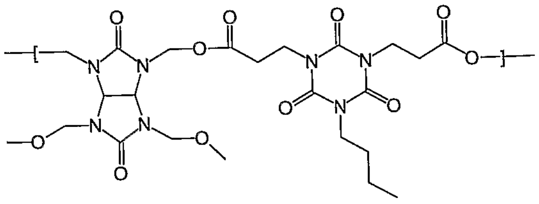


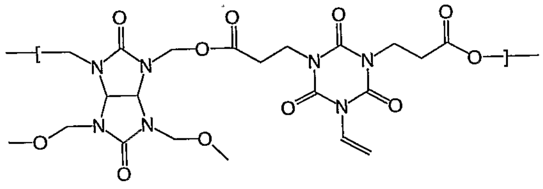






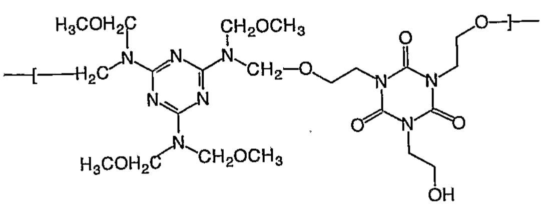


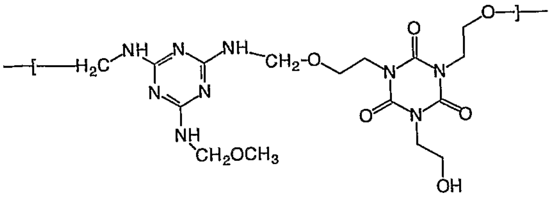


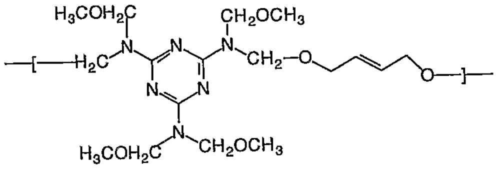


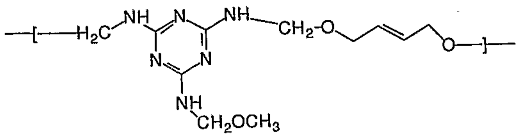
5. The antireflective coating composition of any one of claims 1 to 4 wherein the composition further comprises a polymer that contains an aromatic chromophore.

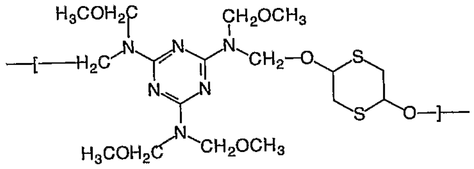
6. A polymer which does not contain an aromatic chromophore comprising a structural unit derived from an aminoplast and a structural unit derived from a diol, triol, dithiol, trithiol, other polyols, diacid, triacid, other polyacids, diimide or mixture thereof, where the diol, dithiol, triol, trithiol, diacid, triacid, diimide, diamide, or imide-amide optionally contain one or more nitrogen and/or sulfur atoms or contain one or more alkene groups, the polymer comprising a repetitive unit selected from

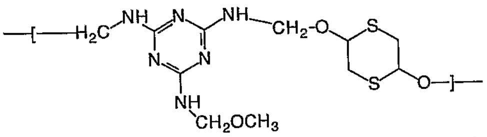


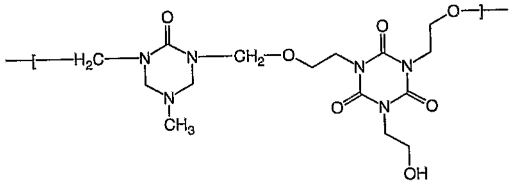


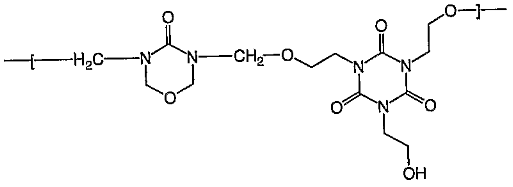


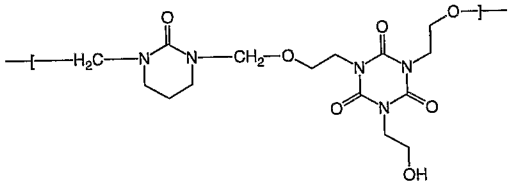


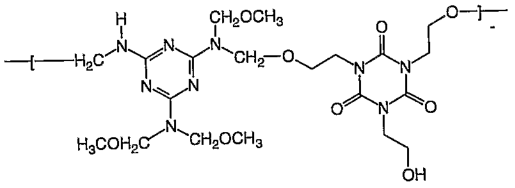


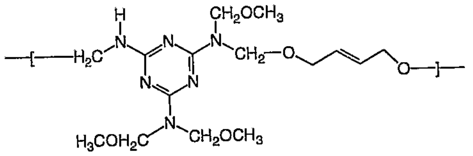


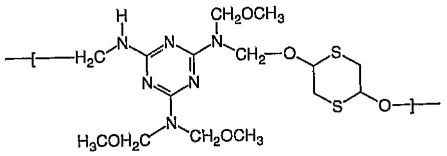


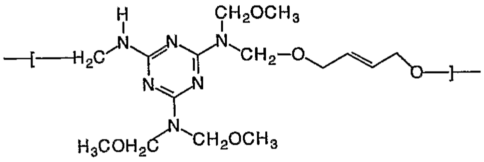


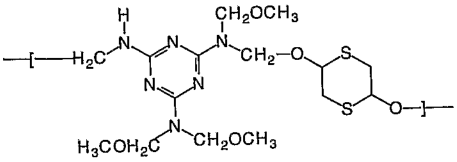


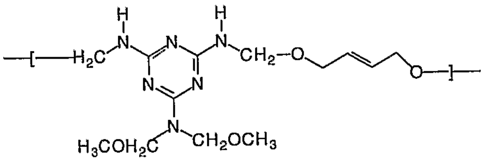


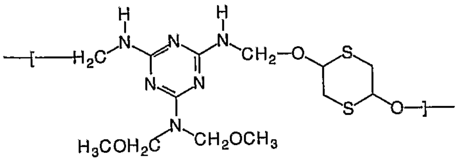


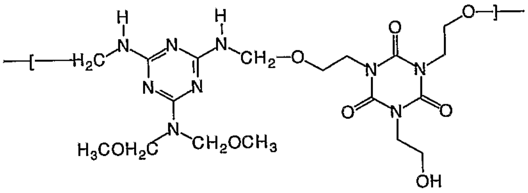


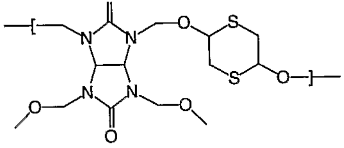


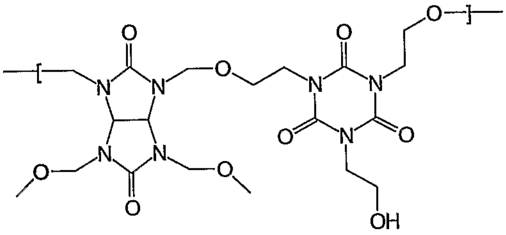


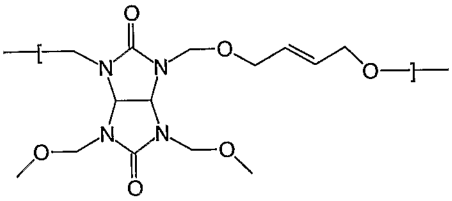


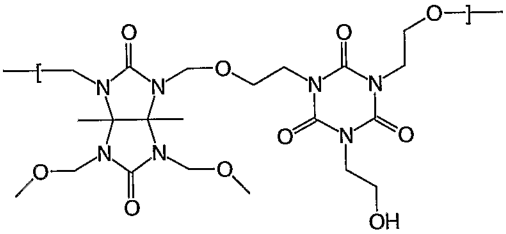


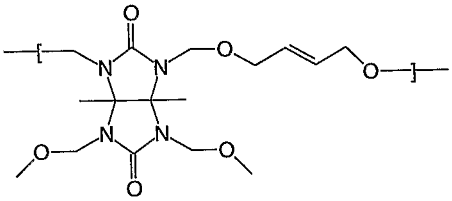


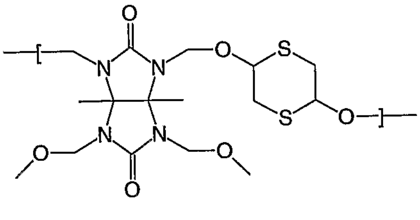


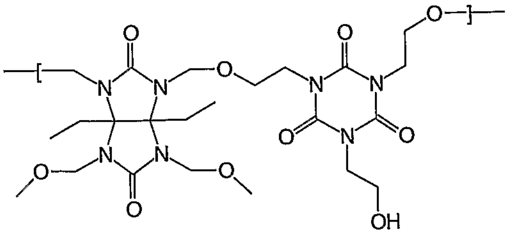


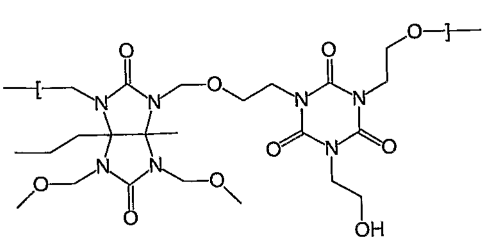


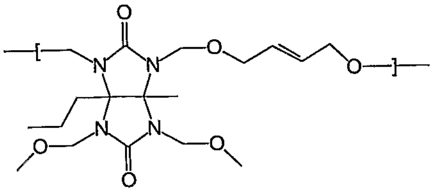


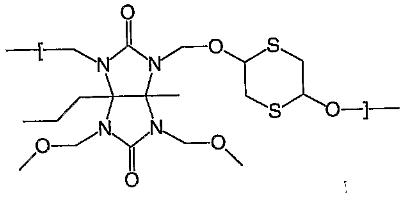


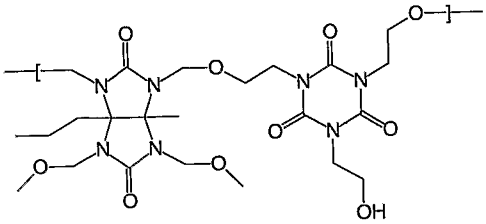


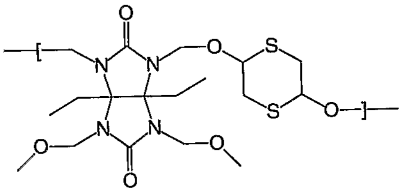


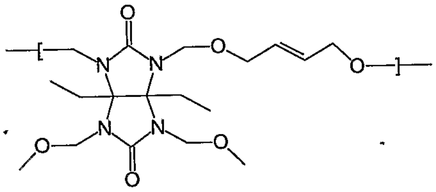


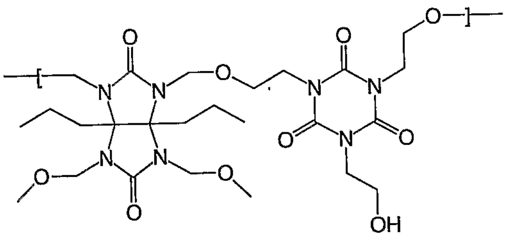


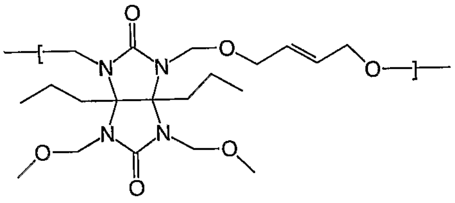


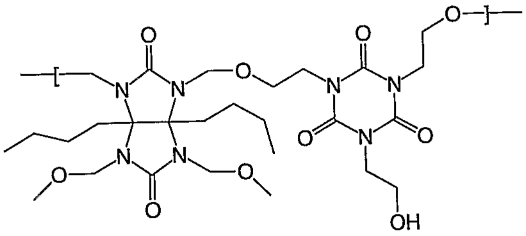


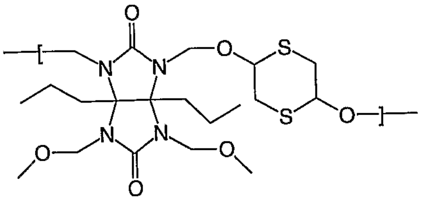


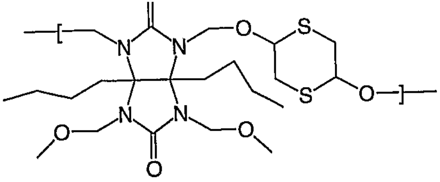


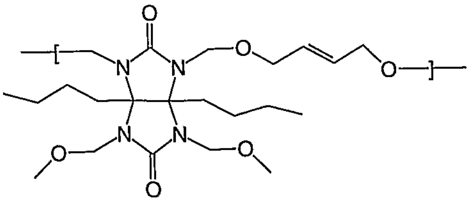


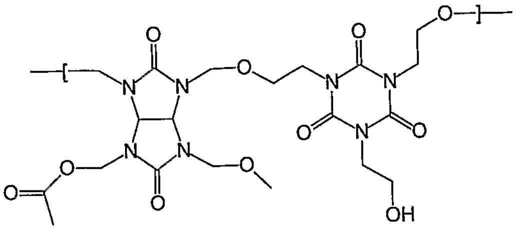








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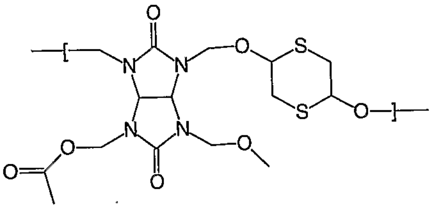
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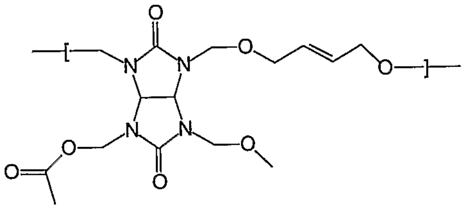
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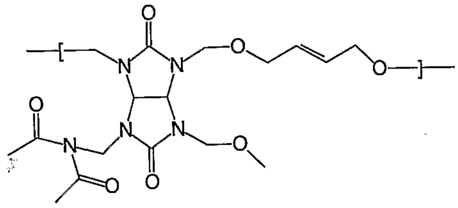
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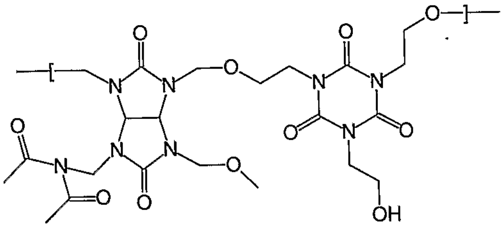
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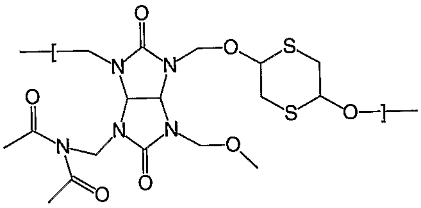
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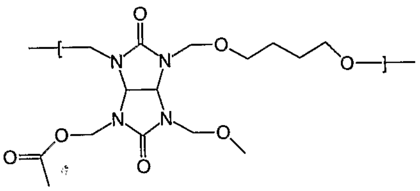
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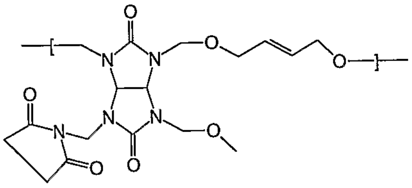
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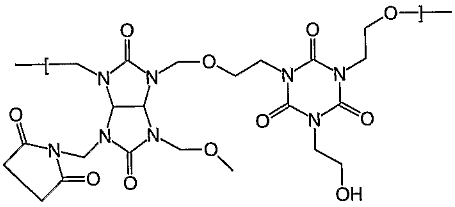
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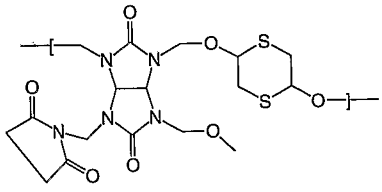
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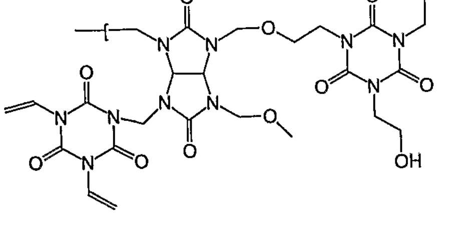
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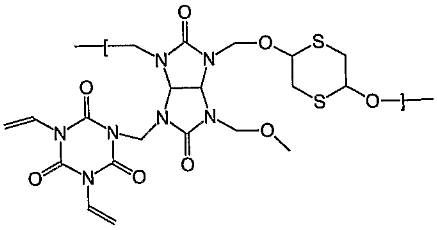
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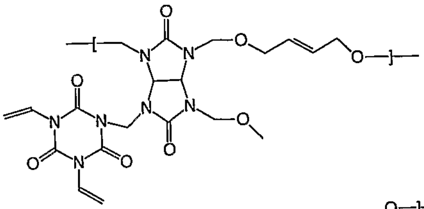
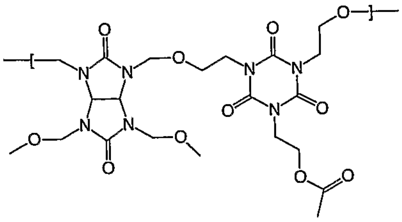
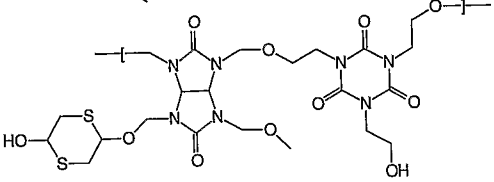
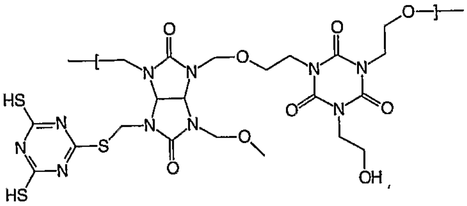
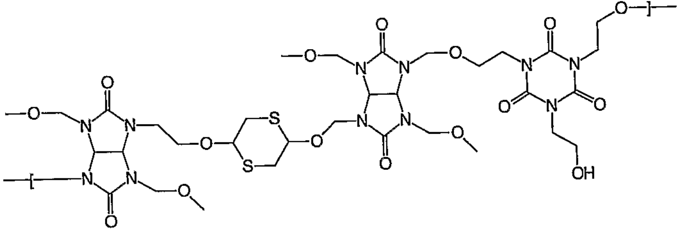
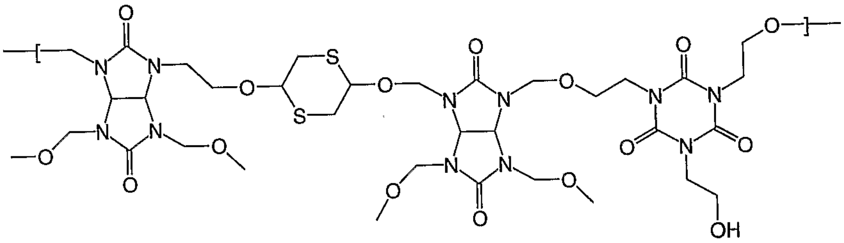


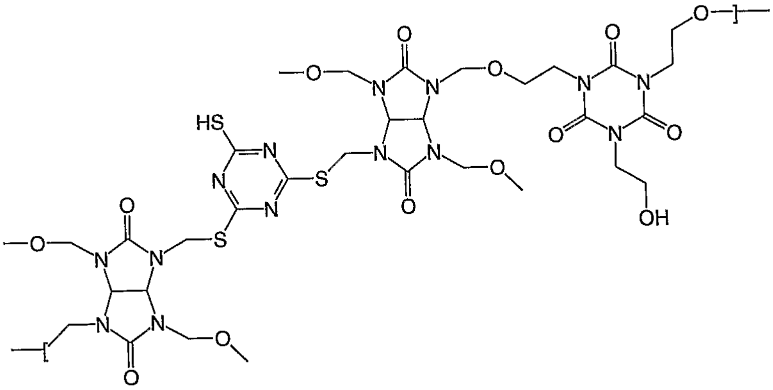


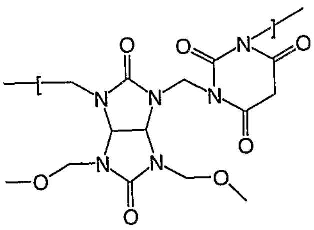


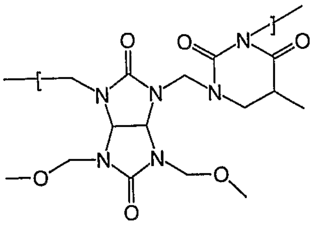


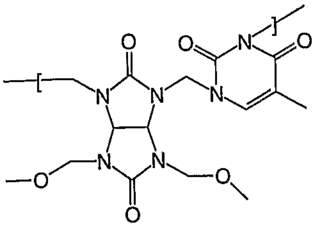


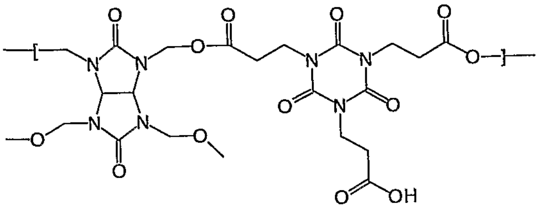


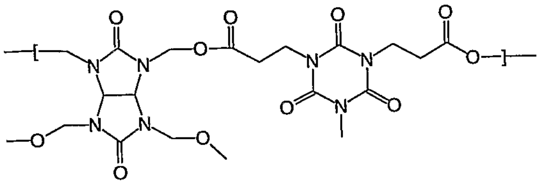


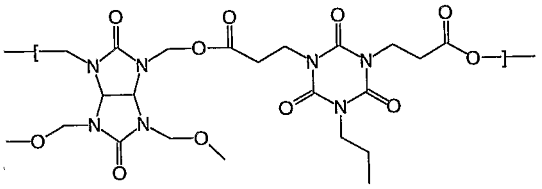


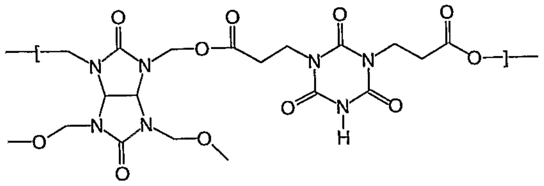


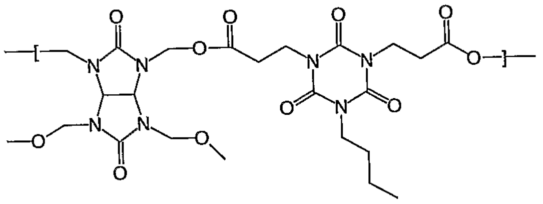


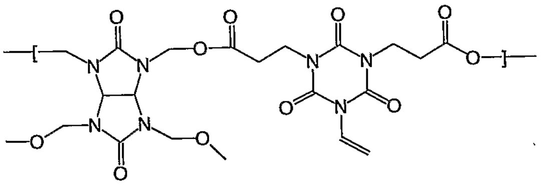












7. A coated substrate comprising a substrate having thereon an antireflective coating layer formed from the antireflective coating composition of any one of claims 1 to 5, where the antireflective coating layer has an absorption parameter (k) in the range of 0.01 ≤ k < 0.35 when measured at 193 nm.

8. A process for forming an image comprising, a) coating and baking a substrate with the antireflective coating composition of any one of claims 1 to 5; b) coating and baking a photoresist film on top of the antireflective coating; c) imagewise exposing the photoresist; d) developing an image in the photoresist; e) optionally, baking the substrate after the exposing step.

9. A process for forming on a substrate an antireflective film and a photoresist film sensitive to an exposure wavelength, comprising:

a) forming an antireflective film on a substrate, where the antireflective film is formed from the antireflective coating composition of any one of claims 1 to 5 where the diol, triol, dithiol, trithiol, diacid, triacid diimide, diamide, or imide-amide in the antireflective coating composition is chosen in such a way that the absorption maximum of the polymer in the antireflective coating composition is less than the exposure wavelength for the photoresist and where the exposure wavelength is between the absorption maximum and the absorption minimum on the long wavelength side of the absorption band of the polymer in the antireflective coating composition, resulting in an anomalous dispersion contribution to the refractive index of the antireflective film that raises the refractive index 'n' of the antireflective film and lowers the absorption parameter 'k' of the antireflective film; and

b) forming the photoresist film on top of the antireflective film.

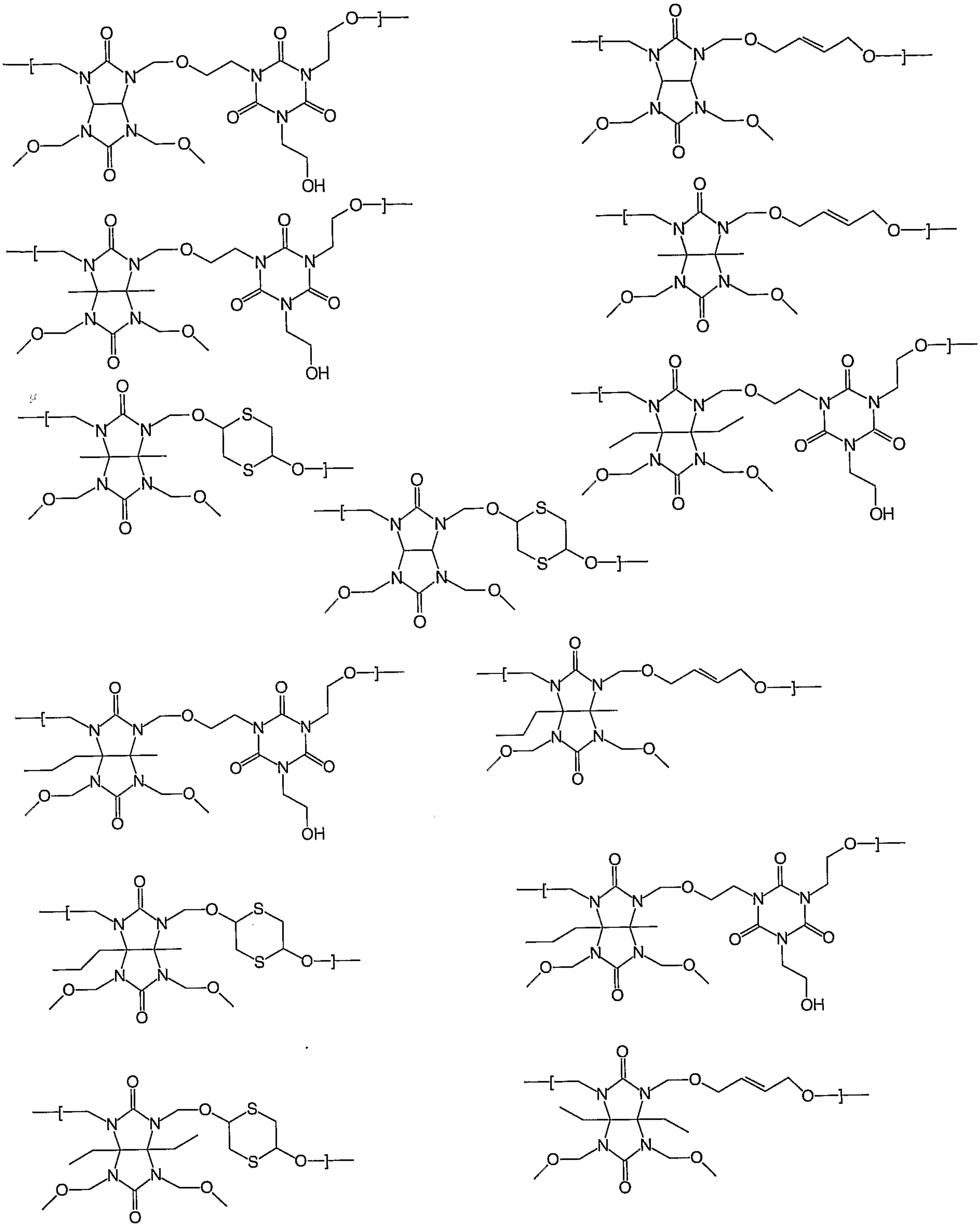
10. The process of claim 9 which comprises

a) forming an antireflective film on a substrate, where the antireflective film is formed from the antireflective coating composition of any one of claims 1 to 5 where the diol, triol, dithiol, trithiol, diacid, triacid diimide, diamide, or imide-amide in the antireflective coating composition is chosen in such a way that the absorption maximum of the polymer in the antireflective coating composition is less than the exposure wavelength for the photoresist and where the exposure wavelength is between the half height of the absorption band of the polymer in the antireflective coating composition and the absorption minimum on the long wavelength side, resulting in an anomalous dispersion contribution to the refractive index of the antireflective film that raises the refractive index 'n' of the antireflective film and lowers the absorption parameter 'k' of the antireflective film; and

b) forming the photoresist film on top of the antireflective film.

11. The process of claim 9 or 10 wherein the diol, triol, dithiol, trithiol, diacid, triacid diimide, diamide, or imide-amide is that of claim 3.

12. The process of any one of claims 9 to 11 wherein for the antireflective coating composition, the polymer comprises a repetitive unit selected from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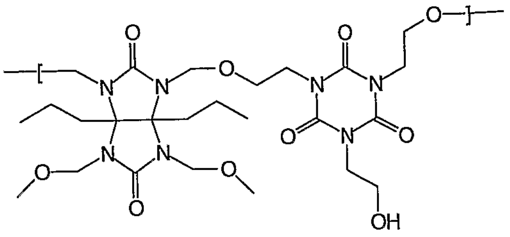

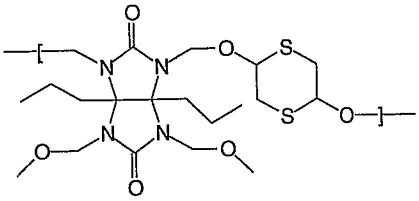

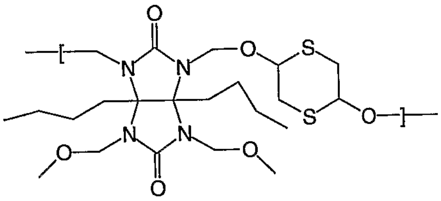

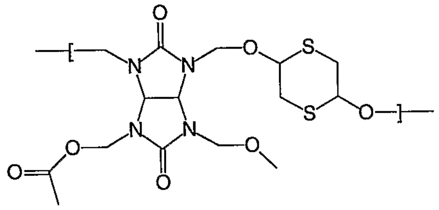

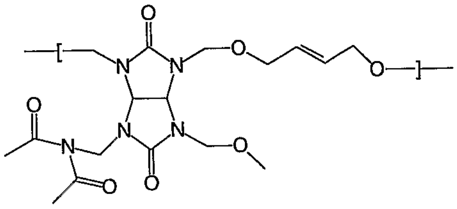

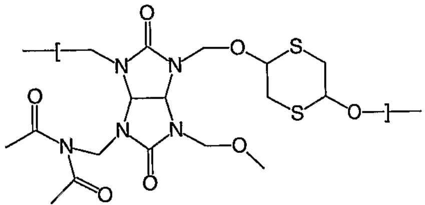

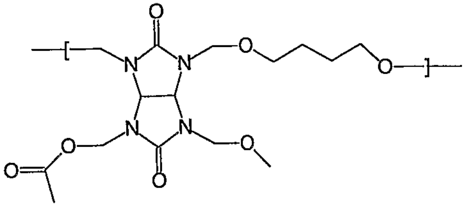

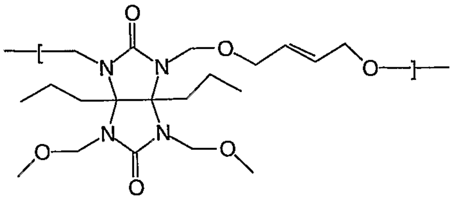

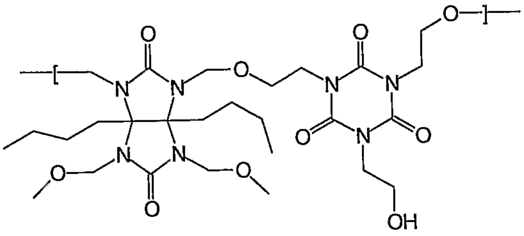

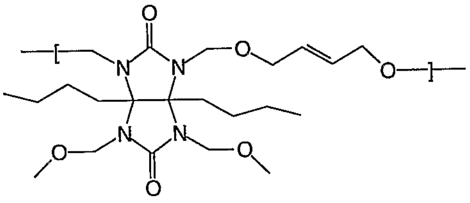

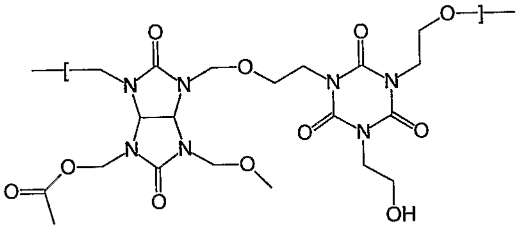

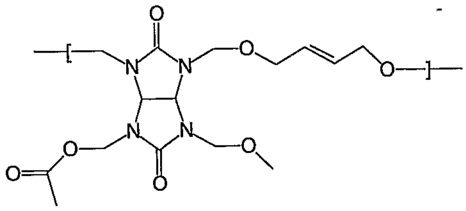

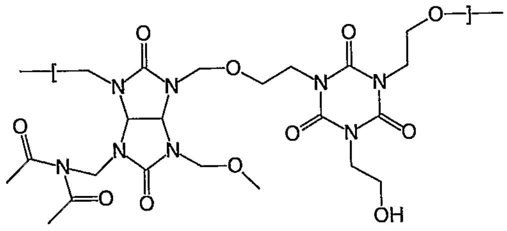

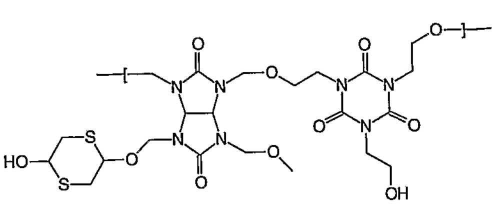

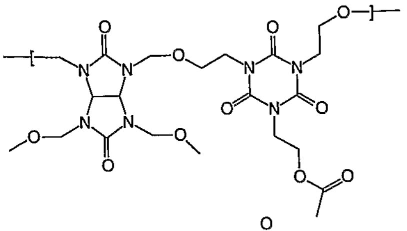

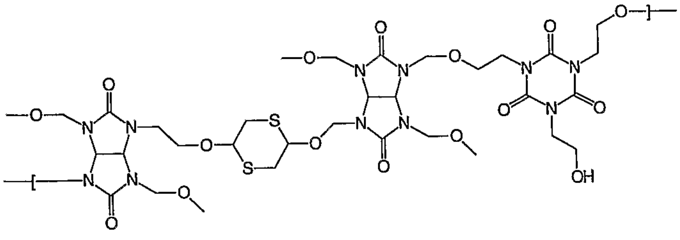

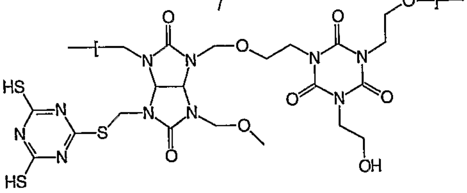

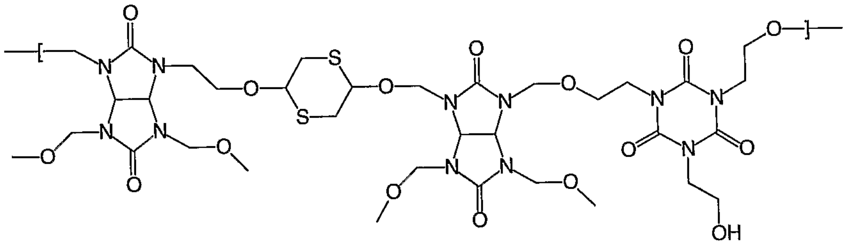

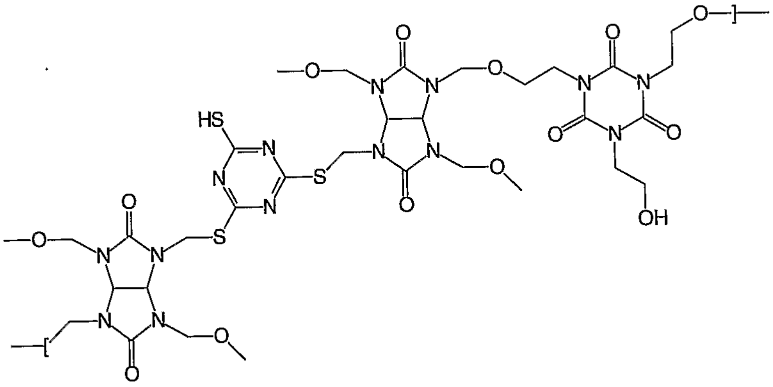

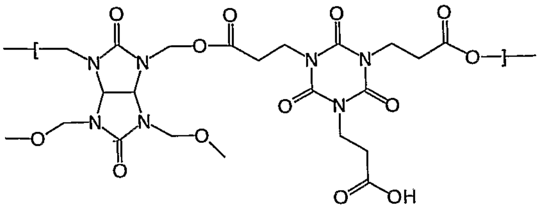

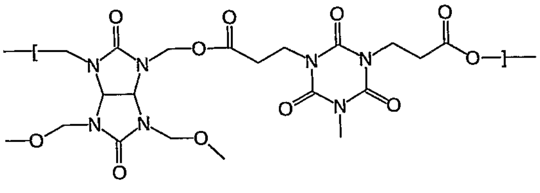

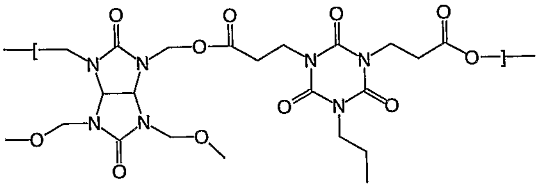

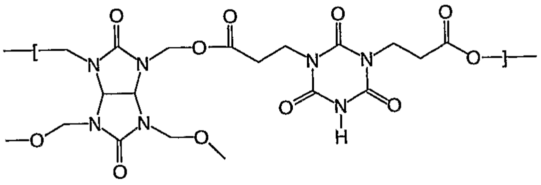

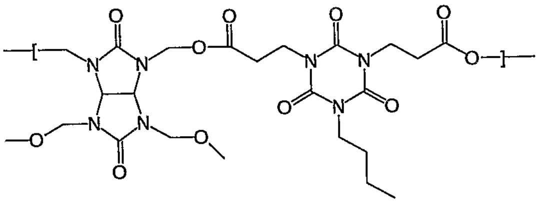

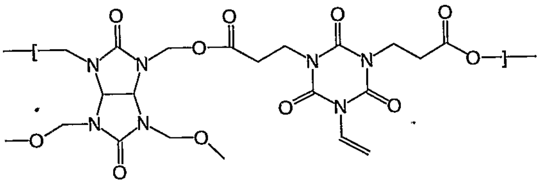

DRAWINGS

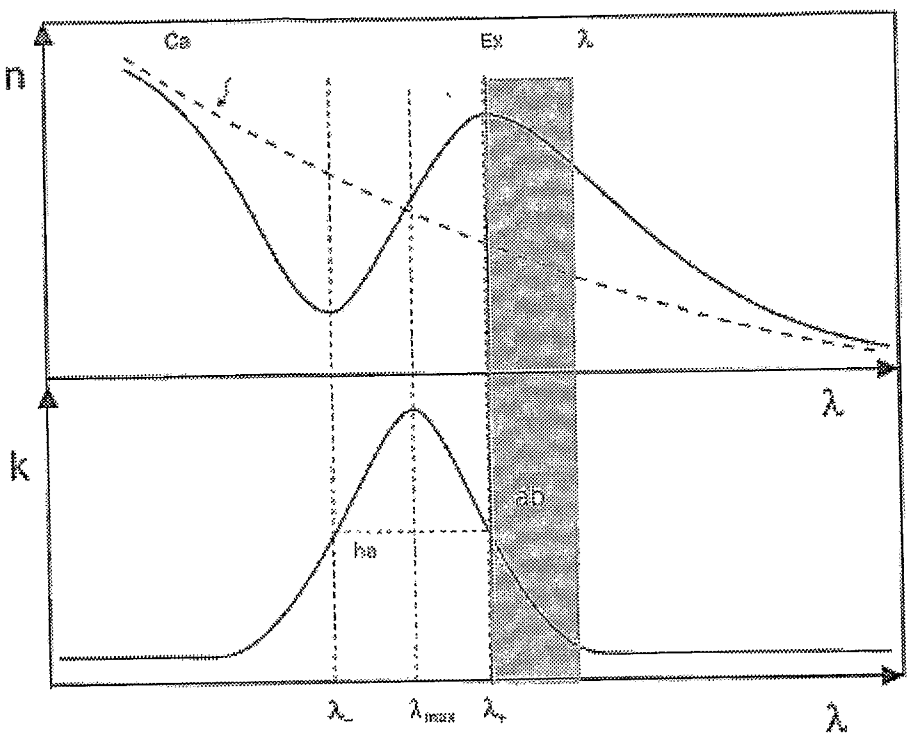

Fig. 1

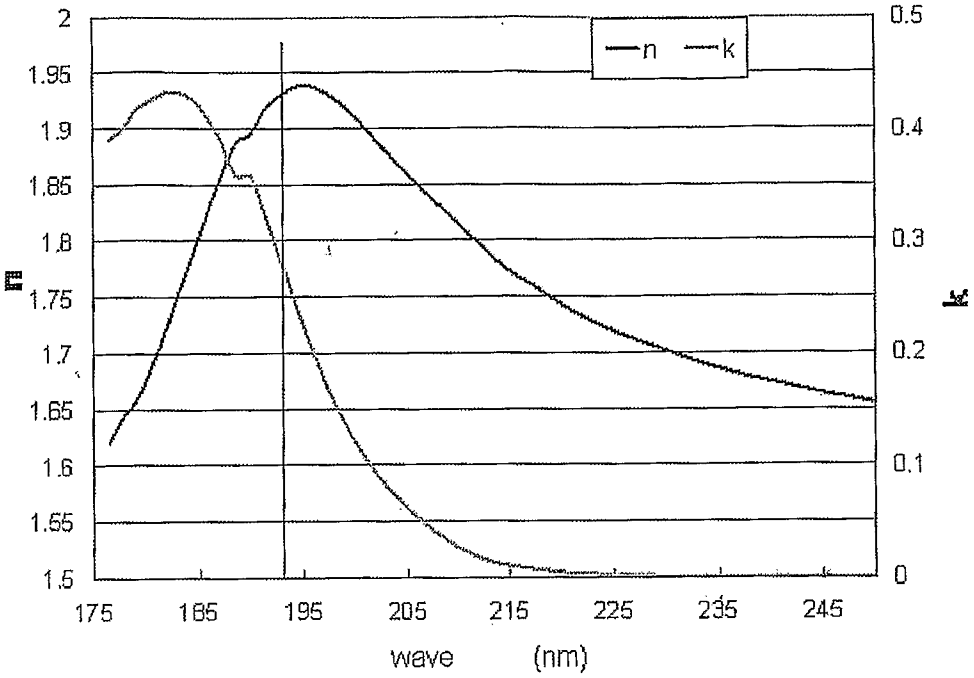
n
k
2
1.95
1.9
1.85
1.8
1.75
1.7
1.65
1.6
1.55
1.5
0.5
0.4
0.3
0.2
0.1
0
175
185
195
205
215
225
235
245
wave (nm)

Fig. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2009/005486

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G18/00 C08L61/00 C09D161/00 C09D161/32 C09D167/00
G03F7/00 G03F7/004 G03F7/09 H01L21/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08G C08L C09D G03F H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2005/097883 A (KING INDUSTRIES INC [US]; HESSELL EDWARD T [US]; ABRAMSHE RICHARD [US]) 20 October 2005 (2005-10-20) paragraphs [0001] - [0089]; claims 1-172; examples -----	1-12
X	EP 1 939 688 A (NISSAN CHEMICAL IND LTD [JP]) 2 July 2008 (2008-07-02) paragraphs [0001] - [0073]; claims 1-12; examples -----	1-12
X	WO 2007/010385 A (AZ ELECTRONIC MATERIALS USA [US]) 25 January 2007 (2007-01-25) page 1, line 6 - page 15, line 31; claims 1-17; examples ----- -/--	1-12

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"&" document member of the same patent family

Date of the actual completion of the international search 21 August 2009	Date of mailing of the international search report 01/09/2009
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Kiebooms, Rafaël

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2009/005486

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 705 519 A (ROHM & HAAS ELECT MATERIALS [US]) 27 September 2006 (2006-09-27) paragraphs [0001] - [0084]; claims 1-10; examples	1-12
X	EP 1 757 986 A (NISSAN CHEMICAL IND LTD [JP]) 28 February 2007 (2007-02-28) paragraphs [0001] - [0030]; claims 1-19; examples	1-12
X	EP 1 560 070 A (NISSAN CHEMICAL IND LTD [JP]) 3 August 2005 (2005-08-03) paragraphs [0001] - [0111]; claims 1-19; examples	1-12
X	US 2006/275696 A1 (ZAMPINI ANTHONY [US] ET AL) 7 December 2006 (2006-12-07) paragraphs [0001] - [0090]; claims 1-10; examples	1-12
X	US 2003/180559 A1 (WAYTON GERALD B [US] ET AL WAYTON GERALD B [US] ET AL) 25 September 2003 (2003-09-25) paragraphs [0001] - [0090]; claims 1-148; examples	1-12
X	US 2005/215713 A1 (HESSELL EDWARD T [US] ET AL) 29 September 2005 (2005-09-29) paragraphs [0001] - [0159]; claims 1-172; examples	1-12
X	EP 1 598 702 A (ROHM & HAAS ELECT MATERIALS [US]) 23 November 2005 (2005-11-23) paragraphs [0001] - [0083]; claims 1-10; examples	1-12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2009/005486

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
WO 2005097883	A	20-10-2005	NONE			
EP 1939688	A	02-07-2008	CN	101268419	A	17-09-2008
			WO	2007036982	A1	05-04-2007
			US	2009117493	A1	07-05-2009
WO 2007010385	A	25-01-2007	CN	101223205	A	16-07-2008
			EP	1915411	A1	30-04-2008
			JP	2009501825	T	22-01-2009
			KR	20080039408	A	07-05-2008
			US	2007020557	A1	25-01-2007
EP 1705519	A	27-09-2006	CN	1847982	A	18-10-2006
			JP	2006341590	A	21-12-2006
			KR	20060101416	A	25-09-2006
EP 1757986	A	28-02-2007	CN	1965268	A	16-05-2007
			WO	2005098542	A1	20-10-2005
			KR	20070007911	A	16-01-2007
			US	2008038678	A1	14-02-2008
EP 1560070	A	03-08-2005	AU	2003271123	A1	04-05-2004
			WO	2004034148	A1	22-04-2004
			JP	4171920	B2	29-10-2008
			KR	20050061523	A	22-06-2005
			TW	280459	B	01-05-2007
			US	2006290429	A1	28-12-2006
			US	2008206680	A1	28-08-2008
US 2006275696	A1	07-12-2006	NONE			
US 2003180559	A1	25-09-2003	US	2004209200	A1	21-10-2004
US 2005215713	A1	29-09-2005	NONE			
EP 1598702	A	23-11-2005	CN	1704455	A	07-12-2005
			JP	2005346051	A	15-12-2005
			KR	20060048011	A	18-05-2006